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ENVIRONMENTAL MONITORING PLAN FOR THE
DOE LIMB DEMONSTRATION PROJECT EXTENSION



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ENVIRONMENTAL MONITORING PLAN FOR THE
DOE LIMB DEMONSTRATION PROJECT EXTENSION

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1. INTRODUCTION

The purpose of this document is to provide guidance for the environmental monitoring required during the DOE LIMB Demonstration Project Extension. This document is required under the terms of the Cooperative Agreement between the Department of Energy and Babcock and Wilcox Company. The DOE project is an extension of an ongoing EPA Limestone Injection Multistage Burner (LIMB) Demonstration. Equipment for this extension is presently being installed at Ohio Edison's Edgewater Power Station in Lorain, Ohio.

The DOE project, as an extension to the EPA LIMB demonstration project, will provide funding to allow investigations of various coals and sorbents, thus extending the technology data base. A second DOE LIMB extension activity is the Coolside Demonstration, which injects sorbent directly into the flue, downstream of the air heater just prior to humidification. For this DOE activity, it is necessary to have the humidifier designed in the EPA LIMB project in operation. The original intent of the EPA humidification effort was to install the humidifier into an existing flue, however, in an effort to assure uninterrupted boiler operation, it was decided to place the humidifier in a bypass duct which can be isolated in the event of start-up problems. The DOE project will provide the bypass. Hence, there will be overlap between the EPA humidification work and the DOE project. Please see Appendix I of this document for further information on the process description.

1.1 PURPOSE

The purpose of the Environmental Monitoring Plan is to:

1. Produce documentation to ensure that demonstration project impacts do not violate applicable standards;
2. Develop a data base to clarify environmental problems related to the LIMB extension technology; and
3. Provide information for future replication of LIMB technology.

1.2 APPROACH

Environmental and human health issues raised by the LIMB Extension Demonstration project were broken down into four broad areas for monitoring and analyses, 1) air, 2) wastewater, 3) solid waste and ground water, and

4) worker health and safety. Monitoring results from these areas will be submitted in unified quarterly and annual reports. Quarterly resource requirements, including travel, sample collection, and analysis and reporting are included for each broad area.

All of the specific environmental and work health and safety parameters to be measured, the point of measurement or sample collection, the frequency of measurement, and quarterly resource requirements for each broad area have been summarized.

An additional option that may be exercised during monitoring is the implementation of pollutant screening methods. The ambient air and wastewater discharge streams would be periodically screened for other pollutants that may be present as a result of the project. A screening method would be performed on each of these two media after each fundamental change in operation, such as the injection of a different sorbent type. Enough samples would be collected and analyzed to determine which pollutants are important for additional monitoring, and to develop a rationale for terminating monitoring for those pollutants that are not significant. An example of such screening is the use of ambient air monitoring canisters that could then be analyzed using the procedures currently in place for EPA's Nonmethane Organic Compound (NMOC) monitoring network. Pollutant screening is not included in the resource requirements section of the plan.

1.3 SCHEDULE

The project is divided into four phases: pre-construction, construction, operation, and post-operation. Pre-construction (baseline) monitoring data, which was collected during Phase I of the EPA LIMB Demonstration Project, will be used as pre-construction monitoring data for the DOE LIMB Extension for most media. For ground water, pre-construction monitoring at the disposal site may be necessary, if no data are currently available.

The modifications to install the LIMB technology are expected to have minimal environmental impacts and thus, construction monitoring is not recommended. Some monitoring will be necessary during construction in order to establish a baseline against which the results of operational monitoring

can be compared. Environmental monitoring of all media will be conducted during the operation phase. Post-operation monitoring will not be necessary except for ground-water monitoring in the vicinity of the ash disposal site. Once the results have stabilized, post-operation monitoring will be discontinued.

Equipment is now being installed at the Edgewater facility for the DOE funded portion of the project. Start-up of the humidifier is scheduled for the first week of August, 1988, followed by completion of the EPA LIMB testing. The DOE LIMB Demonstration Extension covers a period of 43 months, culminating in four months of Coolside Demonstration Testing, followed by 14 months of DOE LIMB Demonstration Testing, with a total of three coals and four sorbents.

1.4 REPORT ORGANIZATION

This document is organized as follows: Section 1.0 is the Introduction and Section 2.0 is the Summary. Air, wastewater, solid waste and ground-water, and worker health and safety monitoring requirements and recommendations are summarized in Sections 3.0, 4.0, 5.0, and 6.0, respectively. Section 7.0 presents data management and reporting requirements, and Section 8.0 summarizes total resource requirements for each broad environmental and worker health and safety area. Finally, Appendix A contains the environmental impact review for the LIMB Demonstration Project Extension required by NEPA, and Appendix B contains copies of test methods for wastewater, ground-water, and solid waste monitoring.

2. SUMMARY

This section presents, in tabular form, a summary of the specific environmental monitoring that will be performed during operation of the DOE LIMB Demonstration Extension Project.

Parameters that must be monitored during the DOE LIMB Extension, and the additional monitoring recommended by this plan are listed in Table 2-1. Parameters common to both EPA LIMB and DOE LIMB Extension are identified. In general, monitoring that is common to both projects are the compliance monitoring required by Ohio EPA, and tests for which baseline values must be established.

Measurement points, sampling frequencies, and resource requirements are also presented in Table 2-1. Resource requirements are presented on a quarterly basis. Initiation costs for establishing reporting programs are covered in the quarterly estimates. However, the costs for implementation of screening methodologies are not included in these resource requirements.

To assist the reader in understanding the following sections, the location of the Edgewater plant in Lorain, Ohio is presented in Figure 2-1. Also, a plot plan of the Edgewater plant is presented in Figure 2-2.

TABLE 2-1. SUMMARY OF ENVIRONMENTAL MONITORING REQUIREMENTS AND
RECOMMENDATIONS FOR THE LIMB DEMONSTRATION EXTENSION PROJECT

Monitoring Recommended During Remainder of:					
Measured Parameter	LIMB ^a	Extension	Point for EMP	Frequency ^b	
<u>AIR MONITORING</u>					
Sulfur dioxide (SO ₂)	X	X	ESP Outlet	Continuous	
Nitrous oxide (NO _x) (as NO ₂)	X	X	ESP Outlet	Continuous	
Oxygen, carbon dioxide (O ₂) (CO ₂)	X	X	ESP Outlet	Continuous	
Carbon monoxide (CO)	X	X	ESP Outlet	Continuous	
Total hydrocarbons (THC)	X	X	ESP Outlet	Continuous	
Particulate matter (PM)	X	X	ESP Outlet	3 runs once every 3 to 6 weeks	
Particle size distribution (PM ₁₀)	X	X	ESP Outlet	3 runs once every 3 to 6 weeks	
Opacity	X	X	ESP Outlet	Continuous	
Air monitoring resource requirements (per quarter): ^{c,d}					
Labor (Hours)				57	
ODC (\$)				75	
Cost Subtotal				<u>2,700</u>	

^a Environmental monitoring parameters measured during the LIMB project are listed only if they are also measured during the LIMB Extension Demonstration project.

^b Several frequencies may be possible, depending on the phase of the project. In general, the highest sampling frequency is listed.

^c Quarterly basis.

^d Air monitoring resource requirements include the cost of preparing a quarterly report and the cost of quarterly ambient air modeling. These requirements are in addition to those covered by the DOE LIMB extension test matrix, thus the cost of the actual sampling and analysis are not included.

TABLE 2-1. SUMMARY OF ENVIRONMENTAL MONITORING REQUIREMENTS AND
RECOMMENDATIONS FOR THE LIMB DEMONSTRATION EXTENSION PROJECT (Continued)

Monitoring Recommended During Remainder of:			
Measured Parameter	LIMB ^a	Extension	Point for EMP
Frequency ^b			
<u>WASTEWATER MONITORING</u>			
pH	X	X	Outfall 601
Daily measurements made on-site (with portable meter).			
Total calcium		X	Outfall 601
Analyze weekly (before and after start-up).			
Resource requirement: ^{c,e}			
Labor (Hours)		42	
ODC (\$)		2,725	
Cost Subtotal		4,400	
<u>SOLID WASTE AND GROUND-WATER MONITORING</u>			
pH, corrosivity, permeability, EP toxicity for RCRA metals, TCLP ^g	X ^f		Ash composite, from ash hopper grab samples
Analyze once, before LIMB Extension start-up.			
pH, corrosivity, permeability, EP toxicity for RCRA metals, TCLP ^g	X		Ash composites, from ash hopper grab samples
Analyze 13 from ash hopper samples after LIMB Extension start-up, one for each sorbent type and coal used, and one duplicate.			
TCLP ^g analytes (see Table 5-3 for complete list)	X ^f		Ash composite, from ash hopper grab samples
Analyze once, before LIMB Extension start-up.			

^aEnvironmental monitoring parameters measured during the LIMB project are listed only if they are also measured during the LIMB Extension Demonstration project.

^bSeveral frequencies may be possible, depending on the phase of the project. In general, the highest sampling frequency is listed.

^cQuarterly basis.

^eIncludes the cost of sample analysis.

^fThese parameters will be analyzed during the EPA LIMB demonstration, i.e., during the DOE LIMB Demonstration Extension project construction phase.

^gToxicity characteristic leachate procedure, a RCRA test procedure designed to simulate leaching in landfills. A different leachate procedure may be substituted, if appropriate.

TABLE 2-1. SUMMARY OF ENVIRONMENTAL MONITORING REQUIREMENTS AND RECOMMENDATIONS FOR THE LIMB DEMONSTRATION EXTENSION PROJECT (Continued)

Monitoring Recommended During Remainder of:			
Measured Parameter	LIMB ^a	Extension	Point for EMP
Frequency ^b			
<u>SOLID WASTE AND GROUND-WATER MONITORING (Continued)</u>			
TCIP ^g analytes	X		Ash composites, from ash hopper grab samples
Table 5-4 analytes	X ^h	X	Monitoring wells at ash disposal site
Resource requirement: ^{c,e}			
Labor (Hours)			42
ODC (\$)			3,700
Cost Subtotal			5,300
<u>HEALTH AND SAFETY MONITORING</u>			
Calcium Oxide (Lime)	X		Personnel off-loading bulk material.
Noise levels	X		Near new air compressor area.
			Minimum of twice during demonstration

^a Environmental monitoring parameters measured during the LIMB project are listed only if they are also measured during the LIMB Extension Demonstration project.

^b Several frequencies may be possible, depending on the phase of the project. In general, the highest sampling frequency is listed.

^c Quarterly basis.

^e Includes the cost of sample analysis.

^f These parameters will be analyzed during the EPA LIMB demonstration, i.e., during the DOE LIMB demonstration Extension project construction phase.

^g Toxicity characteristic leachate procedure, a RCRA test procedure designed to simulate leaching in landfills. A different leachate procedure may be substituted, if appropriate.

^h Table 5-4 analytes will be required to be analyzed on ground water at the chosen ash disposal site, once every six months.

TABLE 2-1. SUMMARY OF ENVIRONMENTAL MONITORING REQUIREMENTS AND RECOMMENDATIONS FOR THE LIMB DEMONSTRATION EXTENSION PROJECT (Continued)

Monitoring Recommended During Remainder of:				
Measured Parameter	LIMB ^a	LIMB Extension	Point for EMP	Frequency ^b
<u>HEALTH AND SAFETY MONITORING (Continued)</u>				
Hazardous components that may be present in ash (see list, Table 6-1)		X	Personnel in pugmill area and maintenance/cleaning areas	Once per quarter, at either measurement point.
Resource Requirement: ^{c,e}				
Labor (Hours)		27		
ODC (\$)		260		
Cost Subtotal		1,900		
TOTAL LABOR (HOURS)		168		
TOTAL ODC (\$)		6,760		
COST TOTAL		14,300		

^aEnvironmental monitoring parameters measured during the LIMB project are listed only if they are also measured during the LIMB Extension Demonstration project.

^bSeveral frequencies may be possible, depending on the phase of the project. In general, the highest sampling frequency is listed.

^cQuarterly basis.

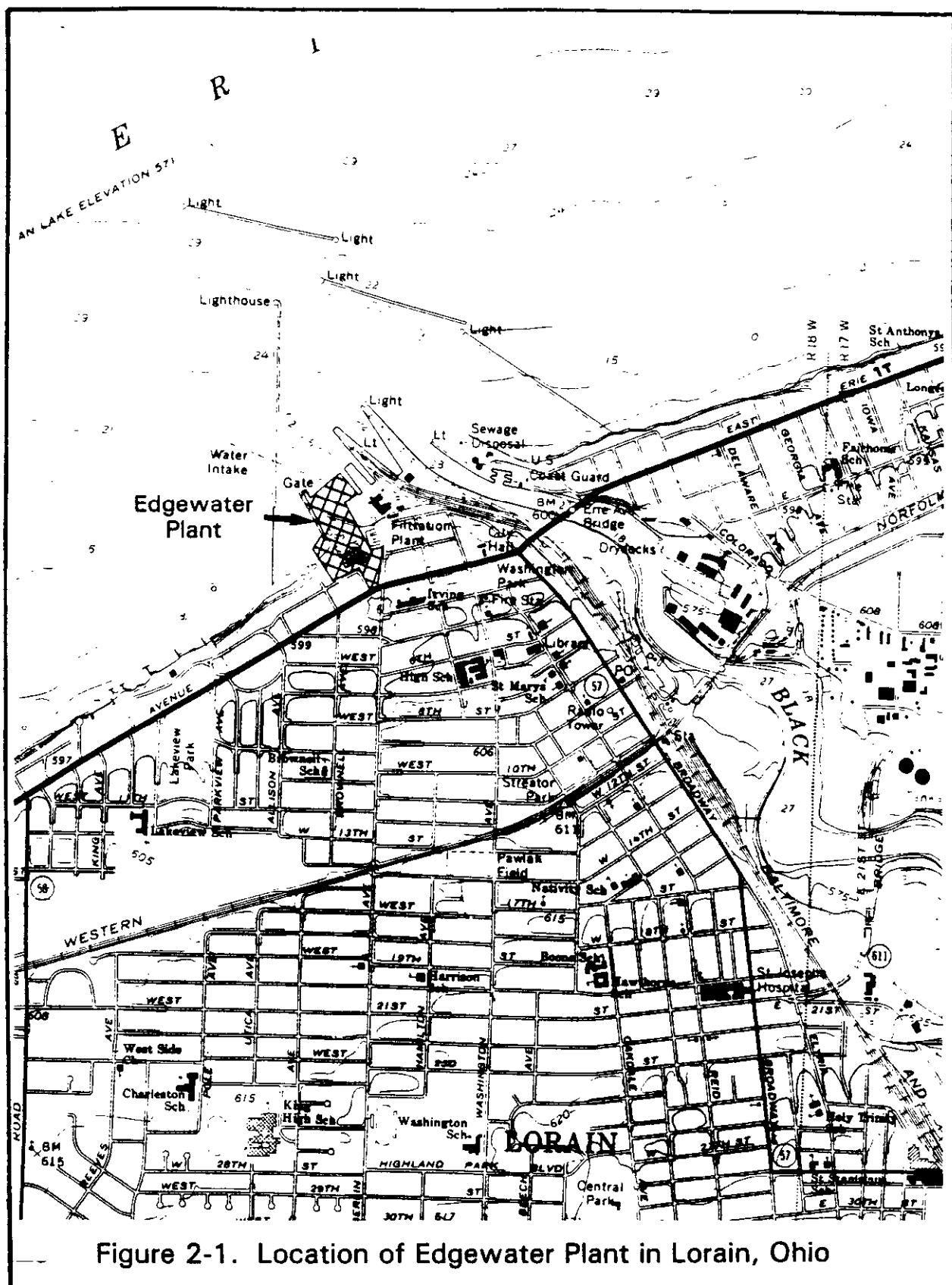
^dAir monitoring resource requirements include the cost of preparing a quarterly report and the cost of quarterly ambient air modeling. These requirements are in addition to those covered by the DOE LIMB extension test matrix, thus the cost of the actual sampling and analysis are not included.

^eIncludes the cost of sample analysis.

^fThese parameters will be analyzed during the EPA LIMB demonstration, i.e., during the DOE LIMB Demonstration Extension project construction phase.

^gToxicity characteristic leachate procedure, a RCRA test procedure designed to simulate leaching in landfills. A different leachate procedure may be substituted, if appropriate.

^hTable 5-4 analytes will be required to be analyzed on ground water at the chosen ash disposal site, once every six months.



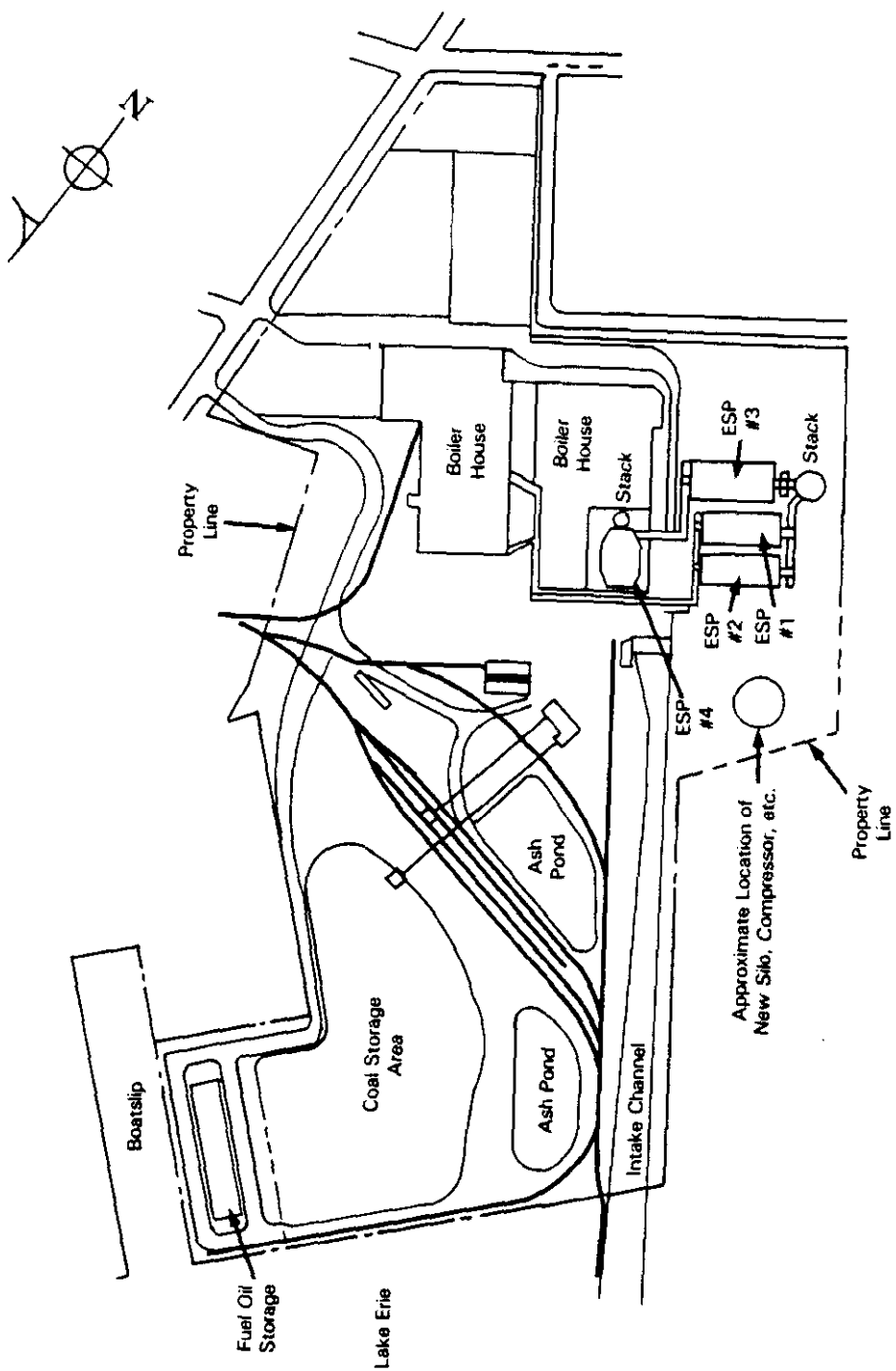


Figure 2-2. Edgewater Plant Site Layout

3. AIR MONITORING REQUIREMENTS AND RECOMMENDATIONS

The air monitoring recommendations of the Environmental Monitoring Plan (EMP) for the LIMB Extension and Coolside projects include specifications for point source emissions, fugitive dust emissions and ambient air concentrations.

The DOE Environmental Monitoring Plan recommends some of the same monitoring (at the ESP outlet only) that will be performed for the test program. Therefore, rather than duplicating sampling efforts, the Environmental Monitoring Plan will evaluate appropriate data from the test program and separately report results in the Environmental Monitoring Plan format. No air monitoring in addition to that already being performed for the test program, is recommended. However, additional data analysis, reporting and ambient air modeling is recommended.

As part of the experimental test matrix, the DOE LIMB Extension and Coolside projects will include continuous monitoring for NO_x, SO₂, CO, CO₂, O₂, and THC, as well as particulate loading and particle sizing measurements. All of these substances will be collected both at the ESP inlet and ESP outlet.

3.1 POINT SOURCES

The Edgewater facility has two point sources. One source is the stack for Unit #4, which is the unit that is being used in the demonstration. The other source is the stack shared by the other two boilers.

3.1.1 Compliance Monitoring

Compliance monitoring is currently required by the Ohio EPA for Unit #4, as specified in their air permit. The permit was recently re-issued on November 6, 1987.

Compliance monitoring is conducted for opacity, particulates, and coal composition. A coal sample collected as the bunker is loaded each day is analyzed daily, and sulfur dioxide emissions are calculated based on the sulfur content of the coal. A stack test for particulate matter is required once every three years. Opacity is monitored continuously by an in-situ opacity monitor. Permit requirements for compliance monitoring are summarized in Table 3-1.

TABLE 3-1. SUMMARY OF CURRENTLY REQUIRED AIR COMPLIANCE MONITORING

Substance	Permit ^a Level (lb/MMBtu)	Frequency of Monitoring	Averaging Approach	Monitoring Method	Duration ^d (yrs)
SO ₂	3.4 ^b	Daily	30 day weighted, rolling average	Analysis of a daily coal sample ^c	3
Opacity	20% ^e	Continuously	6 minute block average	In-situ opacity monitor	3
Particulate Loading	0.1	Once every 3 test runs	Average of 3 one hour test runs	EPA Reference Method 5	3

^alb/MMBtu = pounds of pollutant emitted per 10⁶ Btu actual heat input.

^b30-day weighted, rolling average.

^cA daily composite sample of the coal to be burned each day is collected according to ASTM D2234. The sample is analyzed for ash, sulfur and heat content according to ASTM D3174, D3177, and D3015, respectively. The SO₂ emission rate is calculated from this analysis for each day, and a 30-day rolling weighted average SO₂ emission rate is calculated for each day.

^dThe air permit is granted for 3 years.

^eUp to 60 percent opacity is allowed for a duration of up to six minutes per hour. This regulation is applicable during start-up, once the flue gas temperature reaches 250°F at the ESP inlet.

Although PM monitoring is already required by the State air permit, the frequency of monitoring will be increased to once every three to six weeks (i.e., for each set of new test conditions) for the EMP. Opacity monitoring and coal sampling will continue as before.

3.1.2 Supplemental Monitoring

Supplemental monitoring will be conducted for particulates, PM_{10} , SO_2 , NO_x , and CO. The location, frequency, method, and duration of these tests are presented in Table 3-2. These substances were included either because they are regulated by the State air permit or because they are criteria pollutants under the National Ambient Air Quality Standard (NAAQS). Also, CO_2 and O_2 will be monitored to aid in the interpretation of the SO_2 , NO_x , and CO results.

The test matrix for the LIMB Extension and Coolside projects already includes monitoring for these parameters. Thus, the supplemental monitoring data would be obtained from the test program and reported separately in the EMP quarterly and annual reports.

3.1.2.1 Rationale for Substances To Be Monitored. Emissions from Boiler #13 (Unit #4) are expected to decrease for SO_2 and NO_x and increase for particulates. CO, PM_{10} , and NO_x are also expected to be affected. Expected plant emissions were calculated in the Environmental Information to Fulfill NEPA Information Requirements for the DOE LIMB DEMONSTRATION PROJECT EXTENSION report dated May 20, 1987 (Appendix I).

Left uncontrolled, SO_2 emissions would increase during the LIMB Extension project due to use of coal with a higher sulfur content. However, the LIMB and Coolside technologies are expected to reduce uncontrolled SO_2 emissions below the controlled SO_2 emissions that occur when low sulfur coal is used with the existing control technology (ESP).

Since LIMB and Coolside technologies reduce SO_2 emissions once the coal has been combusted, another approach other than that required by compliance testing will be necessary. The compliance approach is based on the coal sulfur content, and not an analysis of the flue gas. The recommended approach is continuous monitoring of the flue gas from Boiler 13. This monitoring is already included as part of the test plan for the LIMB Extension and Coolside test programs.

TABLE 3-2. SUPPLEMENTAL AIR MONITORING FOR LIMB EXTENSION AND COOLSIDE

Substance	Sampling Location	Frequency of Monitoring	Averaging Approach	Monitoring Method	Duration (yrs)
SO ₂ , NO _x CO ₂ , O ₂	ESP outlet ^b	Continuously	Daily	Extractive CEMs	1.3
Particulate Matter	ESP outlet ^b	Once per condition (every 3-6 weeks)	Average of 3 one-hour test runs per test condition	EPA Reference Method 5	1.3
Particle ^d Size Distribution (PM ₁₀)	ESP outlet ^b	Once per condition (every 3-6 weeks)	Average of 3 one-hour test runs per test condition	Cascade Impactor	1.3

^aLength of the combined DOE LIMB extension and Coolside projects is estimated at 16 months.

^bThe ESP outlet is after I.D. fan, in breeching to stack.

^cSO₂ - EPA Method 6C
NO₂ - EPA Method 3A
CO₂, O₂ - EPA Method 3A

^dPM₁₀ is defined as particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometers.

Additional monitoring will be necessary to document particulate matter emissions. Opacity is required for compliance, but is not directly correlatable to particulate loading. Furthermore, the Method 5 testing requirement for compliance is infrequent (once every three years). A recommended approach, therefore, is to increase the frequency of the Method 5 testing to one series (three test runs) for each test condition (coal/sorbent combination) approximately every 3 to 6 weeks. This will be the frequency used for Method 5 testing for the test program. On-site particulate analysis is also recommended for a quick turn-around of results. This allows for more complete reporting of the emissions monitoring results.

NO_x emissions are expected to be reduced during the LIMB Extension and Coolside programs. During the LIMB program, the existing B and W circular burners were replaced with low-NO_x B and W XCL burners.

The addition of the sorbent is expected to change the particle size (PM₁₀) distribution of the particulate emissions. The pulverized lime may increase the fraction of fine particulate or poorer ESP performance may increase the fraction of larger particulate passing through the ESP. It is uncertain which will be the dominant factor.

CO emissions are expected to increase due to the low-NO_x burners. Low-NO_x burners use staged-air combustion which typically result in higher unburned carbon levels.

3.1.2.2 QA/QC Program. The quality assurance/quality control program will ensure data quality and completeness. The QA/QC program for the LIMB Extension and Coolside test programs will be followed. The QA/QC data will be reported along with the respective emissions data in each quarterly report.

Prior to the test program, the CEM's will be certified according to Performance Specifications 2 and 3 of the New Source regulations to establish that the drift and relative accuracy of the instruments are within prescribed limits. CEM instruments will be calibrated daily, and a daily QC check performed.

For particulate matter sampling, QA/QC procedures will include adjusting the acetone fraction results for the acetone blank and weighing to constant weight (to the nearest 0.1 mg) until three weighings are within

0.5 mg, or one percent of total weight less tare weight. Also, during sampling, isokinetics will be maintained at 100 ± 10 percent, the filter will be maintained at a temperature of $248^{\circ}\text{F} \pm 25$, and the flue gas exiting the ice bath will be maintained below 68°F .

QA/QC procedures for particulate size distribution include those for particulate sampling. In addition, the filtering substrate will be evaluated for weight gain reactions with the flue gas (such as SO_2) and trials runs will be performed and checked for evidence of particle bounce, re-entrainment and overloading.

3.2 FUGITIVES

Fugitive dust at the Edgewater plant can be generated from the plant roadway and parking areas, coal storage pile, coal material handling, ash material handling and ash disposal site. Due to the greater volume of ash generated, additional fugitive dust may be generated during ash handling.

3.2.1 Compliance Monitoring

Existing permits regulate fugitives from plant roadways and parking areas, coal storage pile, coal material handling, ash material handling and the ash disposal site. Compliance regulations are summarized in Table 3-3. Ambient air monitoring by the plant is not required by Ohio EPA and was discontinued by Ohio Edison in 1986.

3.2.2 Supplemental Monitoring

Supplemental monitoring for fugitives is not considered necessary since impacts are expected to be minimal. Existing procedures are expected to control any additional fugitive dusts that may be generated by ash material handling.

The sorbent unloading operation for the test program will be pneumatic, and will include a fabric filter on the silo to control emissions during unloading. Thus, no additional fugitive dusts are expected from this operation.

Vehicular emissions (CO , hydrocarbons, and NO_x) were calculated for the additional traffic for transportation of construction material, coal, sorbent and ash, and impacts to ambient air quality were found to be minimal (see Appendix I). These effects are not considered significant enough to require supplemental monitoring.

TABLE 3-3. SUMMARY OF FUGITIVE COMPLIANCE REQUIREMENTS

Source	Control Methods
Plant Roadways and Parking Areas (Paved and Unpaved Surfaces)	<ol style="list-style-type: none"> 1. Sweeping and flushing of paved surfaces. 2. Watering or chemical treatment. 3. Cover trucks and water-wash vehicle wheels.
Coal Storage Pile to Stationary Conveyor Stacker Bulldozer	Application of water or dust suppression chemicals minimize or eliminate visible emissions. Applied as needed.
Coal Material Handling (coal unloading, con- veying and transfer equipment)	<ol style="list-style-type: none"> 1. Enclosed coal carrying conveyors and transfer points. 2. Routine inspection and repair of enclosures.
Ash Material Handling (flyash conveying, storage silo and load- ing equipment)	<ol style="list-style-type: none"> 1. Flyash watering system operated continuously during truck/loading. 2. Use of flexible chute for tank trucks. 3. Covering of flyash trucks. 4. Water-washing flyash off of truck wheels 5. Operation of equipment to minimize fugitive dust.
Ohio Edison Ash Dis- posal Site (bottom ash and flyash trucks)	<ol style="list-style-type: none"> 1. Applying water to ash at the generator site. 2. Seeding and covering of stored ash. 3. Vehicular traffic speed of 5 to 10 miles per hour. 4. Treatment of unpaved entrance and service roads once every 3 weeks as a minimum.

3.3 AMBIENT MONITORING

Ambient air concentrations of pollutants vary due to several factors including point source emission rates and characteristics, fugitive emissions, and meteorology.

3.3.1 Compliance Monitoring

The Edgewater plant is under the jurisdiction of the National Ambient Air Quality Standards (NAAQS). Regulations exist for SO_2 , CO, TSP, NO_x , photochemical oxidants (ozone) and lead, and are summarized in Table 3-4. The Edgewater plant is located in a designated attainment area for SO_x emissions and a secondary non-attainment area for TSP.

Ambient air monitoring for compliance purposes is conducted by the State according to its State Implementation Program (SIP). The Edgewater plant conducted several years of ambient monitoring, but ceased this monitoring at the end of 1986.

3.3.2 New Regulations and Impact

Effective July 31, 1987, ambient air quality monitoring requirements for PM_{10} (particles less than a nominal 10 micrometers in diameter) were established.

3.3.3 Supplemental Monitoring

No additional ambient monitoring will be necessary for the LIMB Extension and Coolside demonstration projects. Since SO_2 and NO_x emissions from the point source are expected to decrease during the test program, the cost of supplemental ambient air monitoring does not appear to be justified.

It may be as effective to estimate the impact of SO_2 , NO_x , CO and particulates on ambient concentrations by using a dispersion model. The new PM_{10} regulations will be addressed using Method 5 test results, coupled with particle size distribution results. Ohio Edison conducted ambient monitoring from 1983 to 1985 for SO_x and NO_x and from 1983 to 1986 for TSP. Also, stack test data exist for the same ambient monitoring period. New stack test data will be compared to existing stack data to make conclusions regarding the resultant ambient concentrations. Using these data to establish baseline ambient levels, changes in the ambient concentration during the test program will be estimated using dispersion models.

TABLE 3-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS)

Substance	Maximum 24-Hour Concentration Not to Be Exceeded More Than Once Per Year, $\mu\text{g}/\text{m}^3$ (ppm)	Annual Arithmetic Mean, $\mu\text{g}/\text{m}^3$ (ppm)
SO ₂ - primary	365 (0.14)	80 (0.03)
- secondary	1,300 (0.50) (Maximum 3-hour concentration)	
PM - primary and secondary	150	50
CO - primary (no secondary regulation)	10,000 (9) (8-hour average)	
	40,000 (35) (hourly average)	
Ozone - primary and secondary	235 (0.12) (hourly average)	
NO _x - primary and secondary		100 (0.053)
Lead - primary and secondary		1.5 (maximum arithmetic mean averaged over calendar quarter)

Radian will perform the dispersion modeling calculations. Costs presented in Section 8 include dispersion model calculations for each quarter.

4. WASTEWATER MONITORING REQUIREMENTS AND RECOMMENDATIONS

This section discusses the requirements and recommendations for sampling and analysis of existing plant wastewater outfalls during the demonstration project. The outfalls that must be monitored and compliance and supplemental monitoring requirements are identified. Timing of the supplemental monitoring is discussed, and necessary QA/QC procedures are outlined.

4.1 PLANT WASTEWATER DISCHARGES

The wastewater discharge points at the Edgewater Power Generation Station are shown in the water balance diagram in Figure 4-1. The wastewater outfalls and intake structures are listed below:

1. Outfall 001 - consists of condenser cooling water and discharges to Lake Erie;
2. Outfall 002 - consists of intermittent stormwater runoff from the fuel tank spill containment basin area, and also discharges to Lake Erie;
3. Outfall 601 - discharges secondary ash pond effluent. Outfall 601 consists of all major plant wastewater streams and storm water runoff, including runoff from the truck loading and unloading area. This outfall will contain any additional effluents as a result of the LIMB Demonstration Project Extension and discharges to the plant water intake channel;
4. Outfall 606 - consists of intermittent boiler blowdown discharge and drains to the Outfall 001 tunnel.

4.1.1 Compliance Monitoring

The current National Pollutant Discharge Elimination System (NPDES) permit was issued by the Ohio EPA to Ohio Edison for discharging wastewater from the Edgewater Station. This permit requires wastewater monitoring at Outfalls 001, 002, 601, and 606, in addition to the monitoring of two intake points (801 and 802). A summary of current monitoring requirements imposed by this permit on each discharge point is presented in Table 4-1. Compliance monitoring on the outfall that will be impacted by the demonstration project (Outfall 601) includes flow estimation, total suspended solids, and pH sampling and analysis twice per week; and total phosphorus, oil and grease, and arsenic monitoring required on a monthly basis.

Figure 4-1. Diagram of Edgewater Plant Water Flows and Outfalls

TABLE 4-1. CURRENT NPDES PERMIT MONITORING REQUIREMENTS
AT THE EDGEWATER FACILITY

Outfall	Parameter	Method (EPA Storet Number)	Limits		Frequency	Duration
			30-Day	Daily		
001	Flow	50050	--	--	Daily	24-hour total est.
	Total Phosphorous	00665	--	--	Monthly	Grab
	Temperature	00011	--	--	Daily	Continuous
	Total Residual Chlorine	50060	--	0.2	Daily	Grab
	pH	00400	--	6-9	Monthly	Grab
601	Flow	50050	--	--	2/Week	24-hour total est.
	Total Phosphorous	00665	--	--	Monthly	Grab
	Total Suspended Solids	00530	30	100	2/Week	Grab
	Oil and Grease	00556	15	20	Monthly	Grab
	Arsenic	01002	--	--	Monthly	Grab
	pH	00400	--	6-9	2/Week	Grab
606	Flow	50050	--	--	Daily	24-hour total est.
	Total Phosphorous	00665	--	--	Monthly	Grab
	Total Suspended Solids	00530	30	100	Weekly	Grab
	Oil and Grease	00550	15	20	Monthly	Grab
	pH	00400	--	--	Weekly	Grab
002	Flow	50050	--	--	Monthly*	24-hour total est.
	Total Phosphorous	00665	--	--	Monthly*	Grab
	Oil and Grease	00556	15	20	Monthly*	Grab
	pH	00400	--	6-9	Monthly*	Grab

*When discharging

4.1.2 Future Regulations and Impacts

To date, the Ohio EPA is not considering future wastewater discharge or water quality regulations that would impact monitoring of any of these outfalls during the demonstration project.

4.1.3 Supplemental Monitoring

Large quantities of sorbent chemicals will be injected into different parts of the boiler during the demonstration project. These chemicals may include hydrated calcitic lime, hydrated dolomitic lime, calcitic limestone, and dolomitic limestone. Therefore, additional sampling and analysis is recommended of Outfall 601 wastewater. Calcium levels will be monitored, and more frequent pH monitoring will be performed. This supplemental monitoring is recommended to assess the impacts of:

1. The addition of 44 percent CaO to the existing 1,000 GPM wastewater stream from the ash handling system hydraulic exhauster;
2. Additional lime contamination from the truck unloading area during area washdowns and storms; and
3. Non-contact cooling water discharges from the new sorbent feed pump compressor and fluidizing air refrigerant dryer, which may contain lime and limestone contaminants.

In order to establish a baseline data set, supplemental monitoring should begin during the current construction phase. Substances to be tested, test methods (EPA storet numbers), sampling frequency, and duration for supplemental operation monitoring are presented in Table 4-2.

Section 4.2.1 discusses supplemental monitoring during the construction phase of the project.

4.2 TIMING

Supplemental wastewater monitoring will be performed in two phases: construction monitoring and operation monitoring. Because construction of equipment for the LIMB Extension Demonstration and Coolside Technologies is now underway, no pre-construction monitoring will be possible under this plan. Some pre-construction monitoring has already taken place, and those data have been obtained under the current NPDES permit. Additionally, no

TABLE 4-2. SUPPLEMENTAL WASTEWATER MONITORING RECOMMENDATIONS AT THE EDGEWATER FACILITY

Outfall	Parameter	Method (EPA Number)	Description of Process Change	Frequency	Duration
601	pH	00400	a) The concentration of calcium oxide in the existing 1,000 GPM stream from the ash handling system hydraulic exhauster will increase by 44 percent.	Daily	Grab
			b) Additional lime contamination may result from truck unloading area, storm run-off and area washdowns.		
601	Calcium	00916	Noncontact cooling water from new sorbent feed pump compressor and fluidizing air refrigerant air dryer may contain calcium contaminants.	Analyze weekly	Take daily grab, combine into weekly composite.

^aWhen compared to baseline values, these calcium results will indicate the contamination of Outfall 601 water due to sorbent chemicals, if any, in the noncontact cooling water streams. Sorbent chemicals include hydrated lime, hydrated dolomitic lime, calcitic limestone, and dolomitic limestone.

post-project monitoring in addition to the current NPDES requirements is anticipated. However, the results of operation monitoring will clarify the need, if any, for post-project monitoring.

4.2.1 Construction Monitoring

Supplemental monitoring during the construction phase of the demonstration project will be limited to a composite of weekly grab samples of Outfall 601 wastewater, which will be split into two samples, each one analyzed for total calcium (EPA storet number 00916). This analysis, performed using routine laboratory titrametric glassware, will establish a baseline lime/limestone contamination level in Outfall 601 wastewater.

4.2.2 Operation Monitoring

Supplemental monitoring recommended during the operation phase of the demonstration project is presented in Table 4-2. Daily monitoring of pH and weekly monitoring of total calcium is recommended of the Outfall 601 discharge stream.

4.3 QUALITY ASSURANCE/QUALITY CONTROL

Methods for ensuring quality assurance and quality control are incorporated into standard methods used to measure wastewater flows, temperatures, and pollutants. A summary of necessary additional QA/QC procedures is presented in Table 4-3.

TABLE 4-3. QA/QC MEASURES FOR WASTEWATER MONITORING DURING THE LIMB DEMONSTRATION EXTENSION AND COOLSIDE PROJECTS

Parameter	Method (EPA Storet No.)	Instrument	Description of QA/QC Procedure ^a
Total Phosphorus	00665	Block Digester, Auto Analyzer	Calibrate balance every six months unless calibration results show need for more frequent calibration.
Total Suspended Solids	00530	Analytical balance, oven	Calibrate analytical (four-place) balance every six months unless calibration results show need for more frequent calibration. Duplicate analysis on every 10th sample.
Oil and Grease	00550	Separatory funnel	Calibrate analytical (four place) balance every six months unless calibration results show need for more frequent calibration. Duplicate analysis on every 10th sample. Spike a duplicate of every 10th sample with 500 mg motor oil.
Arsenic	01002	Atomic Absorption Spectrophotometer	Calibrate analytical (four-place) balance every six months unless calibration results show need for more frequent calibration. Duplicate analysis on every 10th sample.
Total Calcium	00916	Routine laboratory titrimetric glassware	Calibrate analytical (four-place) balance every six months unless calibration results show need for more frequent calibration. Duplicate analysis on every 10th sample.
pH	00400	pH meter	Calibrate pH meter three times per day, or prior to each use, whichever is more frequent. Use fresh pH 4, 7, and 10 buffer solution for each calibration.

^aRecord all QA/QC data in subcontractor's environmental monitoring data notebook.

5. SOLID WASTE MONITORING REQUIREMENTS AND RECOMMENDATIONS

This section presents the monitoring requirements and recommendations for ash generated during the demonstration project, as well as for ground water in the vicinity of the ash disposal site. Section 5.1 discusses the recommendations for monitoring electrostatic precipitator (ESP) ash during the demonstration project and Section 5.2 summarizes ground-water monitoring requirements. Section 5.3, Timing, outlines what types of monitoring will be required or recommended during the various phases of the demonstration project, and Section 5.4 presents the QA/QC requirements.

5.1 ESP ASH MONITORING

The chemical and physical nature of the Edgewater ESP ash will change considerably after start-up of the LIMB Demonstration Project Extension and Coolside projects, due to the addition of four different types of sorbent into the boiler furnace or flue. Also, the mass rate of ESP ash generated at the station will increase approximately 170 percent. Testing and monitoring are recommended to assess the environmental impacts of these new ash types.

5.1.1 Compositional Monitoring

Composite samples of ESP ash will be collected prior to the demonstration project, and again during the injection of each type of sorbent used during the demonstration. The sample description, frequency of sampling, and sample type necessary for monitoring the composition of the ESP ash, are presented in Table 5-1. Analytical recommendations are presented in Table 5-2.

5.1.2 Leachate Monitoring

The same samples collected for compositional monitoring will also undergo leachate testing. Two leachate procedures will be performed:

1. The EP Toxicity procedure. Leachate from this procedure will then be analyzed for the eight RCRA metals; and
2. The Toxicity Characteristic Leachate Procedure (TCLP). Leachate from the TCLP will be tested for all of the compounds presented in Table 5-3. If appropriate, a different leaching procedure may be used for some of these compounds.

TABLE 5-1. SUPPLEMENTAL ESP ASH SAMPLING RECOMMENDATIONS AT THE EDGEWATER FACILITY

Sample Descriptions	Grab Frequency	Sample Type
Ash generated prior to startup of LIMB extension demonstration. One sample will be composited.	Once per day	Grab sample from each ash hopper, then composite into one sample for analysis.
Ash generated during LIMB extension demonstration project. One sample will be composited for each sorbent-coal combination, for a total of twelve composite samples and one duplicate.	Once per day, during test runs	Grab sample from each ash hopper, then composite into one sample for analysis.

TABLE 5-2. SUPPLEMENTAL ESP ASH ANALYTICAL RECOMMENDATIONS
AT THE EDGEWATER FACILITY

Parameter	EPA Method Number	Instrument Required
Corrosivity	1110	Resin flask with thermowell and automatic temperature control.
TCLP ^a	b	Extraction apparatus.
E.P. Toxicity (RCRA metals)	c	Extraction apparatus, Atomic absorption spectro- photometer.
Permeability	d	d

^aA different leaching procedure may be substituted here for some of the analytes in Table 5-3, if appropriate.

^bMethod is listed in 51 FR 40636, November 7, 1986. See Appendix B for a copy of the complete method.

^cProcedure is outlined in 40 CFR 261, Appendix II. Procedures for analysis of RCRA metals are presented in Appendix B of this report.

^dSpecific method and apparatus will be addressed later. Ash will be stabilized by adding a small quantity of water, and permeability will be performed using the same methods Southern Research Institute (SoRI) used on LIMB process ash by-products generated in a pilot-scale facility.

TABLE 5-3. ANALYSES RECOMMENDED ON LEACHATE GENERATED FROM
THE TCLP PERFORMED ON EDGEWATER ASH SAMPLES

Parameter	EPA Method Number	Instrument Required
pH	9045	pH meter
Chloride	9252	Standard laboratory titrimetric equipment
Copper	7210	Atomic absorption
Iron	7380	Atomic absorption
Fluoride	340.2	pH meter
Potassium	7610	Atomic absorption
Sodium	7770	Atomic absorption
Nitrate (NO ₃)	9200	Spectrophotometer
Sulfate (SO ₄)	9035	Automated continuous flow analytical instrument
Calcium Hardness	309A	Titrimetric equipment
Total Hardness	309A	Titrimetric equipment
P Alkalinity	403	Electrometric titrator
T Alkalinity	403	Electrometric titrator
Acidity	305.1	pH meter
Chemical Oxygen Demand (COD)	410.4	Bench-scale reactor
Total Organic Carbon (TOC)	9060	Bench-scale reactor
Phenols	8040	Gas chromatograph
Total Dissolved Solids (TDS)	208C	Evaporating dishes & analytical balance

5.2 MONITORING WELL TESTING

There has not been a final determination on the waste classification of ash generated during the LIMB Extension Demonstration Project Extension. This ash may either be classified as a solid waste or simply as a waste. The ash classification determines where the ash may be disposed of. Regardless of ash classification, monitoring wells will probably be in place or installed so that ground water in the vicinity of the disposal site can be monitored. The following subsections outline what monitoring will be performed on the ground water collected from these wells.

5.2.1 Compliance Testing

The existing landfill for solid wastes generated at the Edgewater Plant has five active monitoring wells. This landfill, however, will not be used for disposal of ESP ash collected during the demonstration project. Another landfill will be selected for disposal of ash from demonstration testing. Monitoring wells and routine sampling and analysis will be included as a requirement for selection of a disposal site. Table 5-4 lists the substances that will be analyzed and the frequency of sampling and analysis of the monitoring wells at the selected site.

5.2.2 Supplemental Testing

No supplemental testing or analysis is recommended for ground water at the ash disposal site. The Department of Energy/Morgantown Energy Technology Center (DOE/METC) is conducting a research project on the safe disposal of solid wastes from advanced coal combustion processes. Part of this project will be comprehensive ground-water monitoring beneath a test cell that will contain LIMB ash waste from the LIMB Demonstration Project at the Edgewater Power Plant.¹ At this time, it is not known whether the test cell will be located at the same disposal site that will receive ESP ash waste from the LIMB Demonstration Project Extension.

If it is, the ground-water monitoring data generated during this program may be used as an indication of the impacts that LIMB Extension ESP ash is likely to have on ground water beneath the site.

¹Radian Corporation. Field Testing of Disposed Solid Waste From Advanced Coal Processes. Field Test Plan. Radian Document Number 88-218-044-07. Austin, Texas. June 1988.

TABLE 5-4. GROUND-WATER MONITORING THAT WILL BE REQUIRED
AT THE LIMB EXTENSION ASH DISPOSAL SITE

Parameter	Parameter	Frequency
Arsenic (As)	Nitrate (NO ₃)	For all parameters and all wells, sampling and analysis will be conducted on a semi-annual basis (prior to Dec. 15 and prior to June 15 of each year).
Barium (Ba)	Sulfate (SO ₄)	
Cadmium (Ca)	pH	
Chloride (Cl)	Conductivity	
Chromium (Cr)	Calcium Hardness	
Copper (Cu)	Total Hardness	
Iron (Fe)	p alkalkinity	
Fluoride (F)	m alkalinity	
Mercury (Hg)	Acidity	
Potassium (K)	Chemical Oxygen Demand (COD)	
Sodium (Na)	Total Organic Carbon (TOC)	
Lead (Pb)	Phenols	
Selenium (Se)		

5.3 TIMING

5.3.1 Preconstruction Monitoring

As was previously mentioned, construction of equipment for the LIMB Extension and Coolside projects is now underway. Preconstruction monitoring will consist of compiling data already obtained by Southern Research Institute (SoRI) on Coolside-type ash and compiling any available monitoring well data that has already been collected on relevant tests.

5.3.2 Construction Monitoring

Supplemental compositional and leachate monitoring of LIMB ash should begin now, during the current phase of construction. These test parameters, methods, sampling frequency, and sample types desired are outlined in the previous sections.

5.3.3 Operation Monitoring

Monitoring during operation will consist of compositional and leachate testing of ash samples only. These samples will be composites of grab samples collected from the ash hoppers. Twelve composites will be collected, one for each sorbent/coal combination that is demonstrated during operation of the new equipment, as outlined in Table 5-1. Analysis on one of these composites will be duplicated. Therefore, a total of 13 composite ash samples is estimated to be analyzed during operation of the LIMB Extension project.

5.4 QUALITY ASSURANCE/QUALITY CONTROL

Methods for ensuring quality assurance and quality control are incorporated into the standard methods that will be used to analyze both ash compositional samples, leachate samples, and groundwater samples. One blind duplicate sample will be prepared for every ten samples collected, or one for every set of the same type of sample and analyses, if the number of samples in the set is less than ten. This blind duplicate will be split from one of the well-mixed samples in the set, will be numbered, and will be submitted for analysis.

6. HEALTH AND SAFETY CONSIDERATIONS AND MONITORING RECOMMENDATIONS

6.1 PURPOSE AND SCOPE

The purpose of conducting industrial hygiene monitoring is to ensure that the process being evaluated does not cause the overexposure of employees to toxic or harmful agents. The Occupational Safety and Health Act of 1970 requires that employers provide employment that is free of recognized hazards. The Occupational Safety and Health Administration (OSHA) has established exposure standards for the materials to be handled in this process and for noise. As the technology developed in this project may be transferred to other facilities, determining the hazards associated with it will ensure that the Department of Energy and Babcock and Wilcox Company will not incur liability for worker exposure to toxic agents and noise.

The scope of these recommendations are limited to the hazards that may be anticipated during the performance of the Coolside Demonstration. In developing these recommendations, it was assumed that the initial DOE LIMB demonstration project's health and safety hazards were identified, evaluated, and adequately controlled. These recommendations address only the health and safety hazards that are anticipated to be significantly different from those identified in the initial project.

6.2 LIME HANDLING

Lime handling operations present three potential scenarios for employee overexposure to calcium oxide; namely, off loading of bulk raw material, maintenance/cleaning operations, and accidental breakage of a transfer line while under pressure. The OSHA Permissible Exposure Limit (PEL) for calcium oxide is 5 mg/m^3 , while the ACGIH Threshold Limit Value (TLV) is 2 mg/m^3 . Both limits are on an eight hour time weighted basis. It is recommended that the more stringent standard, the TLV of 2 mg/m^3 , be used as a standard to evaluate measured exposures.

6.2.1 Monitoring Recommendations

Monitoring for employee exposure to calcium oxide should be performed early in the project. As the nature of lime handling is not expected to change significantly during the life of the project, an initial monitoring round should prove sufficient to accurately determine and document employee exposure. Exposure levels should be determined for personnel off-loading bulk material.

Worker complaints regarding skin irritation due to lime dust should be monitored continuously during the life of the project.

6.3 ASH HANDLING

Ash handling operations present two potential scenarios for employee overexposure to several different materials. The two possible scenarios would be maintenance/cleaning of, and accidental breakage of transfer lines leading to the pug mill. The composition of the ash, in terms of substances present and particle size distribution, will determine if employee exposure to the ash presents a hazard. The substances that may be present in the ash are presented in Table 6-1. In cases where PELs and TLVs differ, it is recommended that the more stringent of the two be used for a particular compound.

6.3.1 Monitoring Recommendations

Monitoring of employee exposure to ash should be performed early in the project and on at least a quarterly basis thereafter. Monitoring should also be performed if the composition and/or particle size distribution of the ash changes significantly. We recommend that bulk samples be taken of the ash being handled on the day that personnel exposure is measured. By first analyzing the bulk material for the substances listed in Table 6-1, it may be possible to limit the number of substances analyzed for in the personnel samples.

Personnel for which samples should be obtained would include those persons working in the pug mill area and those loading the waste ash into hauling vehicles. If the project will require a planned maintenance/cleaning shutdown, the exposure of persons working on transfer lines and the pug mill, and those engaged in cleaning or repairing bulk storage facilities should also be assessed.

TABLE 6-1
HAZARDOUS SUBSTANCES THAT MAY BE PRESENT IN ASH

Substance	OSHA PEL	ACGIH TLV ^R	NIOSH Method Number (3rd Ed.)	Analytical Technique
Crystalline Silica	Varies with type and % of silica present	0.05 or 0.1 mg/m ³ respirable dust depending on type of silica present	7602	Gravimetric/Colorimetric
Arsenic (Inorganic)	0.010 mg/m ³	0.2 mg/m ³	7300	ICP
Barium (soluble compounds as Ba)	0.5 mg/m ³	0.5 mg/m ³	7056	AA (flame)
Cadmium (as Cd), dust	0.2 mg/m ³	0.05 mg/m ³	7300	ICP
Cadmium (as Cd), fume	0.1 mg/m ³	0.05 mg/m ³	7300	ICP
Chromium (as Cr), soluble salts	0.5 mg/m ³	N.A.	7300	ICP
Chromium (as Cr), metal and insoluble salts	1 mg/m ³	N.A.	7300	ICP
Chromium (VI) compounds, as Cr	N.A.	0.05 mg/m ³	7600	Visible UV
Lead	0.050 mg/m ³	0.15 mg/m ³	7300	ICP
Mercury	0.050 mg/m ³	0.10 mg/m ³	6000	AA (flameless)
Selenium, as Se	0.2 mg/m ³	0.2 mg/m ³	7300	ICP
Nuisance dust, respirable	5 mg/m ³	N.A.	0600	Gravimetric/Selective sampling
Nuisance dust, total	15 mg/m ³	10 mg/m ³	0500	Gravimetric
Sulfur dioxide	13 mg/m ³	5 mg/m ³	6004	IC

6.4 SULFURIC ACID HANDLING

The primary health and safety considerations for sulfuric acid handling center around basic safety parameters such as spill control, bulk off loading safety and tank and line labeling.

6.4.1 Monitoring Recommendations

The OSHA PEL and ACGIH TLV are both 1 mg/m^3 on an eight hour time weighted basis. Because people typically will not tolerate this level of exposure except for short lengths of time due to eye, nasal, and airway irritation, sulfuric acid monitoring will probably not be necessary. However, if workers complain of irritation, their exposures should be measured at the earliest available opportunity.

6.5 NOISE

It is not known if noise levels associated with the air injectors will be significantly higher than those associated with boilers.

6.5.1 Monitoring Recommendations

The noise levels associated with the air injectors should be measured and compared with those associated with normal boiler operation. This monitoring should be performed throughout the project. Areas with noise levels significantly higher than normal (+3 dBA), potentially around the air compressors and booster fans associated with the lime feed system and additive injection system, should be posted with signs recommending that hearing protection be used.

6.6 TRUCK TRAFFIC

This project is expected to require from 22 to 24 additional truck trips per day. This will not have a significant impact on employee health and safety. It will increase the risk of accidental injury due to the numbers of vehicles involved, but, if normal safe driving procedures are followed, this increased risk will be kept to a minimal, or no effect, level.

6.7 DOCUMENTATION

The OSHA Medical Records Access Rule (29CFR 1910.20) requires that the employer of employees sampled preserve and maintain exposure records for 30 years. This rule also requires that employees, or their designated representative, have access to exposure records within 15 days after the request for access is made.

7. INFORMATION MANAGEMENT AND REPORTING

The Information Management and Reporting System will address management techniques and procedures, as well as compliance and supplemental monitoring activity data flows and procedures.

7.1 MANAGEMENT AND PROCEDURES

The proper performance of management and procedures for reporting environmental monitoring data will be the responsibility of the Radian Project Director. Data gathering and reporting will emphasize confirmation of results by employing a system of review and checking as shown in Figure 7-1.

The data management team is located within the project organization under Task 6, as shown in Figure 7-2. Environmental data management activities will be scheduled as part of the overall project management activities.

Available resources for data reduction include experienced data collection and reduction staff members. In terms of hardware, a minimum of two microcomputers located in the Radian CEM trailer will be on-site to aid in data reduction. In addition, associated and backup equipment will be available. Most of this equipment currently exists on-site and was used for the EPA LIMB project.

Data will be collected, stored, analyzed and reported during the construction and operating phases of the program. Environmental monitoring data will be summarized on a quarterly basis and submitted by February 1, May 1, August 1, and November 1. Daily results will be reduced by the end of the following day.

QA/QC results will be summarized and explained with the respective sampling data. All original data sheets and reported laboratory results will be stored and copies will be used for calculations and evaluation. Originals will be identified as such.

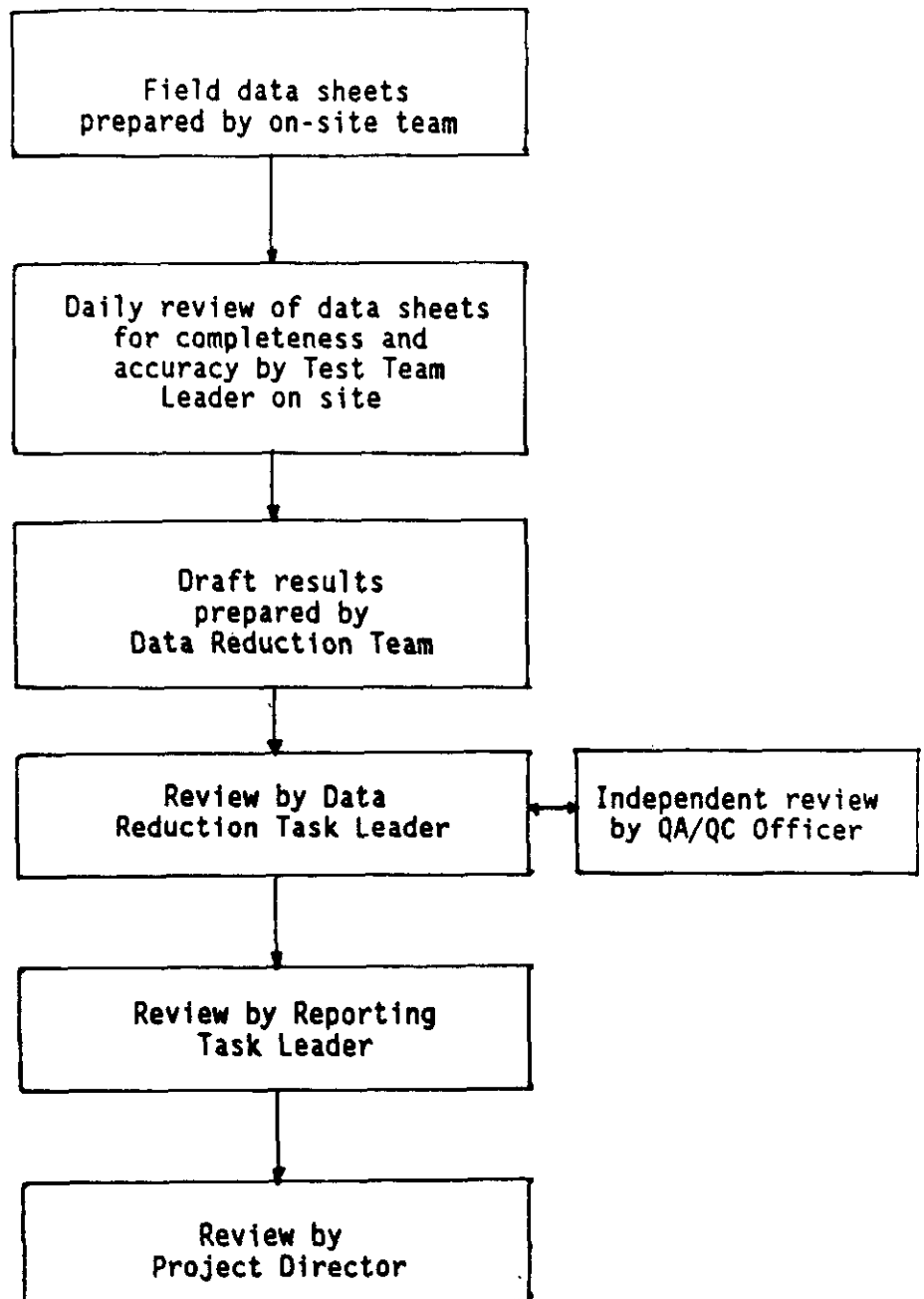


Figure 7-1. Review Scheme for Data Management

TABLE 7-2. SUMMARY OF WASTEWATER AND SOLID WASTE DATA
ELEMENTS TO BE COLLECTED, STORED, AND ANALYZED (Continued)

Data Element	Recording Method	Analysis	Method ^b Number	Analytical Instrument ^b
<u>Supplemental Monitoring - ESP Ash Leachates</u>				
TCLP Analytes ^d	Record in logbook and computer	Off-site	d	d
E.P. Toxicity Analytes:	Record in Logbook and computer	Off-site	--	---
Arsenic (As)			7060	AAS
Barium (Ba)			7080	AAS
Cadmium (Cd)			7130	AAS
Chromium (Cr)			7191	AAS
Mercury (Hg)			7470	AAS
Lead (Pb)			7420	AAS
Selenium (Se)			7740	AAS
Silver (Ag)			7760	AAS

^bIn some cases, it may be necessary to substitute an alternate EPA-approved method due to matrix interferences or high detection limits.

^dSee Table 5-3 for the list of EPA-approved methods and analytical instruments used for the TCLP analytes.

TABLE 7-3. SUMMARY OF HEALTH AND SAFETY DATA ELEMENTS
TO BE COLLECTED, STORED, AND ANALYZED^a

Data Element	Recording Method ^b	Analyses
Noise Levels	Record in logbook and computer	On-site readings
Calcium Oxide Dosimeters	Record in logbook and computer	Off-site Lab
Ash (Nuisance Dust) Dosimeters	Record in logbook and computer	On-site Lab
Bulk Ash Samples, Analyzed for:	Record in logbook and computer	Off-site Lab
Arsenic		
Barium		
(Soluble Compounds as Ba)		
Cadmium (as Cd), Dust		
Chromium (as Cr), Soluble Salts		
Chromium (as Cr), Metal and		
Insoluble Salts		
Chromium (VI) Compounds, as Cr		
Lead		
Mercury		
Selenium, as Se		
Sulfur Dioxide		

^aSee Table 6-1 for sampling and analytical methods and instrumentation.

^bEmployee exposure measurements and accompanying documentation will be submitted to B&W for their employee exposure records.

TABLE 7-4. SUMMARY OF DATA FLOWS FOR SAMPLING AT THE ESP OUTLET
USING IBM PC BASIC AND LOTUS SOFTWARE AND RADIAN PROGRAMS

Substance	Frequency of Measurement	Measurement & Analytical Method	Estimated Overall Precision (+ %)	Estimated Overall Accuracy (+ %)
SO ₂ (CEM)	Continuous	EPA Method 6C	5 ^a	20 ^b
NO _x (CEM)	Continuous	EPA Method 7E	5 ^a	20 ^b
O ₂ , CO ₂ (CEM)	Continuous	EPA Method 3A	10 ^a	20 ^b
CO (CEM)	Continuous	EPA Method 10A	10 ^a	20 ^b
THC (CEM)	Continuous	EPA Method 25A	10 ^a	20 ^b
Particulate loading (Method 5)	3 runs once every 3-6 weeks	EPA Method 5	11 ^c	10 ^c
Particle size distribution (Cascade Impactor)	3 runs once every 3-6 weeks	Cascade Impactor (Andersen)	11 ^c	10 ^c
Opacity	Continuous	40 CFR Part 60.7 and 60.13		

^aThe estimated overall precision is based on coefficients of variation from previous test programs. Coefficient of variation (CV) for daily analysis of control sample is defined as:

$$CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\%$$

^bThe estimated overall accuracy is based on relative errors from previous test programs. Relative error (%) for audit analyses or reference method tests, is defined as:

$$\text{error} = \frac{\text{Measured Value} - \text{True Value}}{\text{Actual Value}} \times 100$$

^cPrecision and accuracy based on EPA collaborative tests.

NOTE: The definitions of coefficient of variation and relative error are from the Guidelines and Specifications for Preparing Quality Assurance Project Plans, U.S. EPA.

The chain-of-custody of samples and data is illustrated in Figure 7-3.

The CEMs sample acquisition system is illustrated in Figure 7-4.

7.2.2 Wastewater and Solid Waste Monitoring

The data flow, from monitoring sources to final data processing and analysis for all wastewater, ash, and collected ground-water samples, will follow this sequence:

1. Collect and label sample(s);
2. Log time, date, location, sample type, sample identifier, and tests to be run in bound sample log book;
3. Log initials of sampler in log book;
4. Fill out chain of custody form(s).

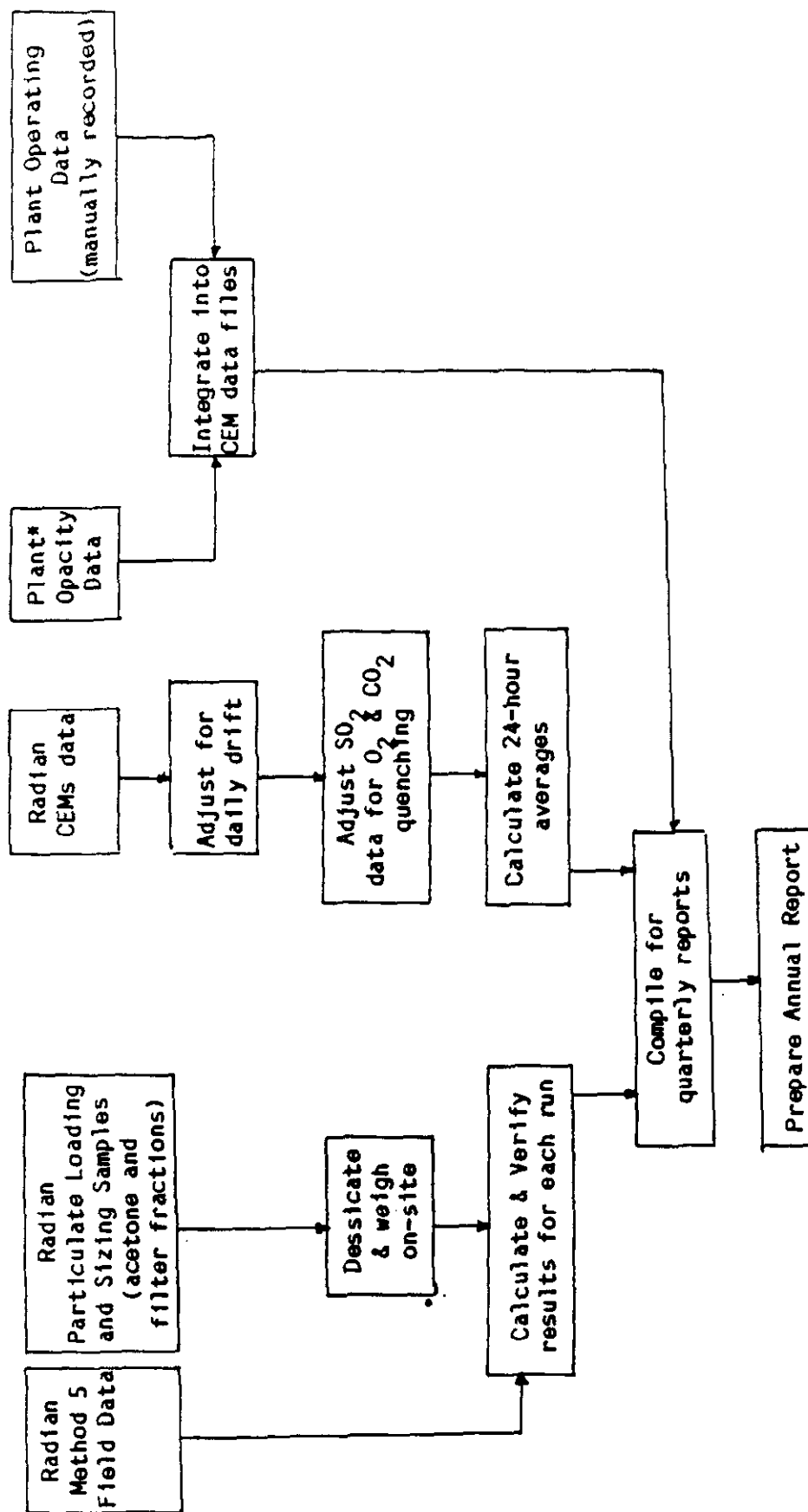
If the samples collected are grab samples being composited, the sequence ends when the composite is complete. For completed composite samples and other grab samples, the following additional steps must be followed:

5. Submit sample(s) for analyses, along with chain of custody form(s);
6. Receive hardcopy of analysis and QA/QC results from laboratory with final custody form, and log date of receipt in log book;
7. Record analysis results in log book, if tests run are required compliance tests;
8. Enter data into computer for final analysis and reporting; and
9. Store hardcopy in permanent file.

7.2.3 Health and Safety Monitoring

The data flow from dosimeters, bulk samples, and noise level monitoring sources to final data processing and analysis will follow the sequence below:

1. Collect and label samples, or take readings;
2. Log date, time, location, reading or sample type, sample identifier, and tests to be run on sample in a bound log book.
3. Log initials of sampler/data-taker in logbook;
4. Fill out chain of custody forms;
5. Submit samples for analysis, along with chain of custody forms;
6. Receive hardcopy of analysis and QA/QC results from laboratory with final custody form, and log date of receipt in log book.
7. Record analysis results in log book and computer for later quarterly and annual reporting, and compare to TLVs and PELs.
8. If higher than TLVs or PELs, alert B & W at once.



*Compliance data

Figure 7-3. Chain-of-Custody of Samples and Data

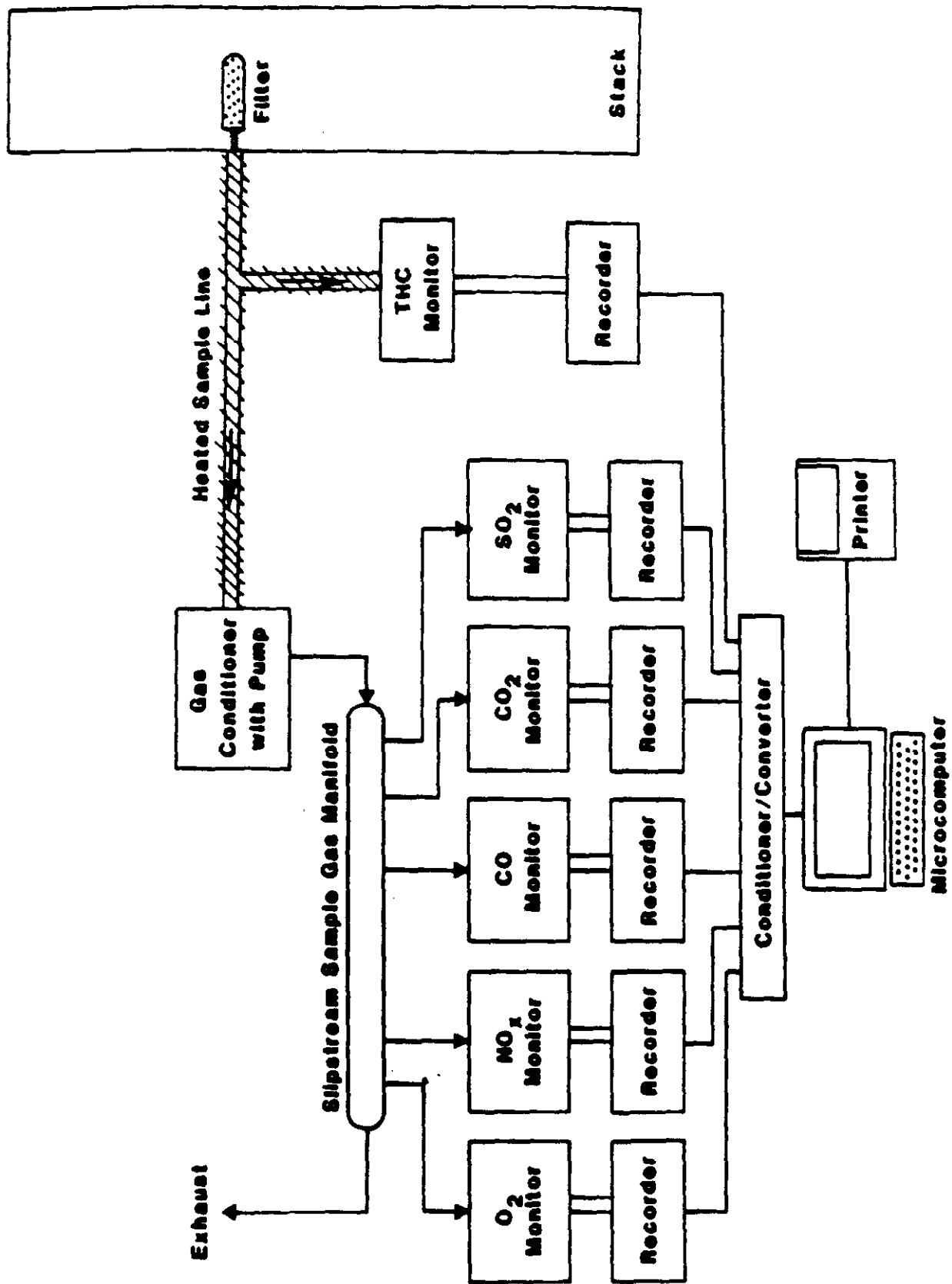


Figure 7-4. CEMS Sample Acquisition System

7.3 DATA MANAGEMENT AND REPORTING TECHNIQUES

A microprocessor-controlled data logging system is used for the CEM data. A Compaq Deskpro 286 Personal Computer^R with 640K of internal memory is used. This computer system will also be used to store and access the wastewater, solid waste, and health and safety monitoring data. Data is stored on a hard disk and backed up on high density floppy disks. Files are backed up at the end of each test run. An index is kept of the contents of each disk.

IBM PC^R compatible software is used to reduce all of the environmental monitoring data and produce summary graphs and charts. Near-letter quality printouts can be obtained from the wide-carriage Epson FX286e^R printer. Software typically used includes MS-DOS (version 3)^R, Basic 3.0^R, Lotus 1 2 3^R, Harvard Presentation Graphics^R, and DBase III^R.

The on-site locations where the originals of the data sheets are filed and samples are stored are locked when Radian personnel are not on-site.

All files related to the supplemental monitoring will be retained permanently unless specifically requested by the client.

Particulate filters and catches and all solid waste (ash) samples will be retained until the reports are finalized. They may be retained longer if follow-on work is likely, requiring these samples (i.e., such as metals analysis).

At the completion of the test program, all files will be stored on high density floppy disks with a backup for each disk. Hard copies of each file will also be retained. Disks will be stored in a temperature-controlled, dust-restricted environment.

7.4 REPORTING FREQUENCY

Quarterly reports will be submitted by February 1, May 1, August 1, and November 1. The fourth quarterly report will include an annual summary. Reports will be submitted to Dr. Earl Evans at the Department of Energy's Pittsburgh Energy Research Center.

The content of the quarterly reports is outlined below:

1. Highlights:

- What happened during quarter;
- Recommendations for changes;
- Action items identified.

2. Project status:
 - Plant description;
 - Design and operational changes;
 - Activities during quarter.
3. Source monitoring:
 - Discharge source monitoring (gaseous, aqueous, solid streams, and fugitives);
 - Pollution control unit monitoring;
 - Products and by-products monitoring;
 - Plant operating condition monitoring.
4. Ambient monitoring:
 - Air;
 - Surface water;
 - Ground water;
 - Soil;
 - Ecological;
 - Additional;
 - Plant operating conditions.
5. Compliance monitoring status.
6. QA/QC results.
7. Monitoring problems/recommendations for change:
 - Problems encountered/envisioned;
 - Solutions;
 - Recommended changes.

Appendices:

- Detailed source monitoring data;
- Detailed ambient monitoring data;
- Compliance monitoring report;
- QA/QC results;
- Modifications/changes to sampling and analytical methods;
- Events that could have impacted monitoring results;
- Other attachments.

8. ENVIRONMENTAL MONITORING PLAN RESOURCE REQUIREMENTS

Quarterly resources, in addition to those required for compliance and those already planned for the LIMB test program, are summarized in Table 8-1. For the air emissions, additional resources are required for dispersion modeling and preparing the reports. For wastewater, solid waste, and worker health and safety, additional resources are required for sampling and analysis, reporting, and travel. Resources used to implement phases of the Environmental Monitoring Plan will be reported on a quarterly and annual basis.

TABLE 8-1. QUARTERLY RESOURCE REQUIREMENTS FOR ENVIRONMENTAL MONITORING
IN ADDITION TO THOSE REQUIRED FOR THE LIMB PROJECT^{a, b}

Description of Task	Labor			Overhead Direct Cost (\$)	Total Cost (\$)
	Senior Engineer (hr)	Engineer (hr)	Secretary (hr)		
Air Monitoring:					
SO ₂ , NO _x , CO, CO ₂ , O ₂ , THC, particulate loading, and particle size reporting	0	13	16	25	895
Ambient air dispersion modeling and reporting	<u>0</u>	<u>22</u>	<u>6</u>	<u>50</u>	<u>1,750</u>
SUBTOTAL	0	35	22	75	2,700
Wastewater monitoring and reporting	0	36	6	2,725	4,400
Solid waste monitoring and reporting	0	36	6	3,700	5,300
Health and safety monitoring and reporting	21	0	6	260	1,900
TOTAL	21	107	40	6,760	14,300

^aA hearing conservation program is not included in these resource requirements.

^bResource requirements shown include the preparation of a quarterly report every three months, and an annual report yearly.

APPENDIX A

ENVIRONMENTAL INFORMATION TO FULFILL NEPA INFORMATION
REQUIREMENTS FOR THE DOE LIMB DEMONSTRATION PROJECT EXTENSION

DCN: 87-262-011-03

ENVIRONMENTAL INFORMATION TO FULFILL
NEPA INFORMATION REQUIREMENTS
FOR THE DOE LIMB DEMONSTRATION
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1.0 INTRODUCTION

The purpose of this document is to present a self-contained volume of environmental information on the DOE LIMB Demonstration project Extension. The information will be used to facilitate DOE's preparation of the environmental documents required to comply with the National Environmental Policy Act of 1969 (NEPA). The DOE project is an extension of an ongoing EPA Limestone Injection Multistage Burner (LIMB) Demonstration. The EPA Demonstration is presently in the construction phase at the Edgewater facility of Ohio Edison. Efforts to develop, install and operate a flue gas humidifier system upstream of the electrostatic precipitator (ESP) in a bypass flue to primarily improve sulfur dioxide capture and secondly to improve precipitator performance is currently in the design engineering phase under a modification to the EPA base LIMB contract. Therefore, information concerning all potential environmental impacts is not available at this time. Estimates of impacts have been made as appropriate.

The DOE project, as an extension to the EPA LIMB demonstration project, will provide funding to allow investigations of various coals and sorbents thus extending the technology data base. A second DOE LIMB extension activity is the Coolside demonstration which injects sorbent directly into the flue downstream of the air heater just prior to humidification. For this DOE activity, it is necessary to have the humidifier, designed in the EPA LIMB project, in operation. The original intent of the EPA humidification effort was to install the humidifier into an existing flue. However, in an effort to assure uninterrupted boiler operation, it was decided to place the humidifier in a bypass duct which can be isolated in the event of start-up problems. The DOE Project will provide the bypass. Hence, there will be overlap between the EPA Humidification work and the DOE project.

The humidification portion of the EPA LIMB project will be carried out in the last 4 months of the project. Since humidification is part of the LIMB program, there would be no additional impacts attributable to the humidification portion of the DOE Coolside project. For the purposes of this

document, the assumption is made that impacts attributable to the humidification will be quantified and considered.

The EPA limestone injection multi-stage burner (LIMB) demonstration project is already underway with respect to low NO_x burner operation. However, the sorbent injection system is under construction. The efforts described in this document cover an expansion of the LIMB project to determine the performance of LIMB over a wide range of coals and sorbents and to determine the performance of the Coolside sorbent injection process.

LIMB has the potential to bring uncontrolled plants into compliance with state and federal regulations, promulgated as of January 1, 1986, at much lower cost than the installation of expensive wet scrubbers or even at lower cost than switching to low-sulfur coals imported from other regions. Coolside is a low-cost retrofit technology with the capability of reducing SO_2 by injecting sorbents and additives into the flue gas duct just prior to humidification. Both these demonstrations will be conducted at Ohio Edison Company's Edgewater Station, Unit No. 4, in Lorain, Ohio.

The proposed work falls under DOE's Clean Coal Technology Program "emerging clean coal technologies" under categories "in boiler control of oxides of sulfur and nitrogen," and "post-combustion cleanup." The EPA LIMB testing program is scheduled to start in mid-May 1987 and will run for 12 months. The DOE funded portion of the project will be conducted over 43 months consisting of the Coolside demonstration with 4 months of testing and the DOE LIMB demonstration of three further coals and four sorbents consisting of 14 months of testing. This document is organized as follows: Section 1.0 is the Introduction, Section 2.0 is the Summary of the Environmental Analysis, and Section 3.0 presents Existing Site Characteristics. A Project Description is contained in Section 4.0, and Consequences of the Project are discussed in Section 5.0. Regulatory Compliance is contained in Section 6.0, and Information Necessary for Evaluating Impacts to Water Resources is contained in Section 7.0.

2.0 SUMMARY OF ENVIRONMENTAL ANALYSIS

The purpose of this chapter is to present a brief summary of the environmental, health, safety and socio-economic information and analysis for the LIMB Demonstration Extension Project. A tabular summary of the impacts relative to the existing situation at the Edgewater station is presented in Table 2-1. The majority of the impacts are short-lived, i.e., will disappear once the project has been completed. As the table shows, the impacts from the project will be largely beneficial or negligible with one exception: the impacts of the solid wastes produced by the demonstration. The demonstration project will produce some 20 to 30 acre-feet of solid waste requiring disposal. However, it should be noted that this material is classified as non-hazardous and that this material can be readily stabilized and has low permeabilities after curing. If this material is properly impounded in a licensed state landfill operating under the Ohio state requirements, it should have little or no impact on the environment.

The proposed project presents very low environmental health and safety risks during construction, operation and disposition. There are no unique ecological communities being threatened by the project. Water emission streams will not significantly increase the volume of existing power plant streams and can be readily treated.

No new environmental permits will be required as a result of this project, but some changes in existing permits will be required. A permit variance has been requested and granted to burn high-sulfur coal during the baseline demonstration phases of the project. A change has been requested in the facility's NPDES permit to account for the additional wastewater emission sources entering the ash ponds which will be subsequently discharged from that outfall. The solid wastes will be managed in a state-licensed landfill.

None of the additional waste streams generated from the facility will be uncontrolled. When burning low-sulfur coals, the SO_x and NO_x emissions will be reduced over what they would be in the absence of the LIMB extension and

TABLE 2-1. ENVIRONMENTAL IMPACTS OF PROPOSED ACTION

	LIMB Extension	Coolside
ENVIRONMENTAL EMISSIONS		
<u>Air</u> - SO _x	+2	+2
- NO _x	+2	+2
- Particulate	-2	0
<u>Waste water</u>	-2	-2
<u>Solid waste</u>	-3*	-2
ENERGY	-1	-1
HEALTH AND SAFETY	-1	-1
WATER RESOURCES	-1	-1
SOCIO-ECONOMIC IMPACTS		
<u>Employment</u>	+1	+1
<u>Irreversible commitment of resources</u>	-1	-1

Key

- + Beneficial impact
- Adverse impact
- 0 No impact
- 1 Negligible impact
- 2 Small impact
- 3 Moderate impact
- 4 Large impact
- * Long term impact

Coolside technologies. The NO_x emissions will be reduced during all testing by the low NO_x burners to be used throughout testing. Particulate loading to the ESP may increase during portions of the LIMB extension test. However, the ESP used by the facility is oversized and is expected to be able to achieve the emissions level prescribed in the permit. The combination of the oversized precipitator and humidification which serves to increase SO_2 removal in LIMB technology, to improve resistivity of the particulate, to reduce flue gas volume and to enhance ESP efficiency should achieve prescribed emissions levels.

The pH and suspended solids levels in the ash pond effluent may be increased by the LIMB and Coolside technologies. However, provisions have been made for acid addition to maintain the pH within the permit limits.

The most significant unresolved issue for the LIMB Demonstration Project Extension is the choice of solid waste disposal site. Until the site is identified the complete significance of potential environmental and socio-economic impacts cannot be determined. Environmental impacts from the chosen disposal site with respect to air emissions and runoff can be readily controlled and are expected to be insignificant.

Another area of uncertainty involves performance of the ESP with increased solid loading in the flue gas. Baseline particulate tests were in compliance. However, comparisons of the mass loadings indicate that the ESP was apparently not performing up to specifications. This may have been the result of measuring condensable material in addition to particulate. Periods of non-compliance with the particulate emissions limits, if they occurred, would be short-lived and once detected, corrective actions would be taken immediately to rectify the problem. Humidification for improved SO_2 removal would then be incorporated into the test program and provide improved precipitator performance.

3.0 EXISTING SITE CHARACTERISTICS

3.1 SITE LOCATION

The LIMB Demonstration Project Extension will be performed at Ohio Edison Company's Edgewater Station. The station is located adjacent to Lake Erie, approximately 25 miles west of Cleveland and 90 miles east of Toledo, Ohio (see Figure 3-1). It is located in northeastern Ohio in Lorain County at 200 Oberlin Avenue, Lorain, Ohio 45052 (see Figure 3-2). Map coordinates are 82 degrees, 11 minutes east and 41 degrees, 28 minutes north.

3.2 SITE DESCRIPTION

The Edgewater facility has a total net demonstrated power capability of 214 MWe and consists of three pulverized coal fired boilers serving two turbines and two oil fired combustion turbine generators. The station is used to provide power to the Ohio Edison System. Edgewater Unit No. 4 has a rated capacity of 105 MWe and is presently burning eastern bituminous coal with a medium sulfur content of 1.5 to 1.7 percent. The boiler can consume 42.5 tph of coal. Total station coal consumption is 1,400 tpd with all units in operation. The coal is delivered by truck, and normally 45 to 50 trucks arrive at the facility per day. Unit No. 4 is equipped with a new oversized Lodge-Cottrell electrostatic precipitator. The facility utilizes 110 million gpd of once-through cooling water taken from Lake Erie and discharges 1.1 million gpd of wastewater to the lake from the fly ash ponds. Fly ash and bottom ash are trucked to a 56-acre landfill located in Lorain County.

The Edgewater Station occupies 21 acres of a manmade promontory or peninsula on the lake shore at the mouth of the Black River. The facility is bounded to the northeast by a filtration plant and railroad spur and to the south and southwest by residential areas. These areas are within 200 feet of the power building. Several schools are located within a half-mile of the facility to the south. Access to the site is limited to two entrances, both of which are from Oberlin Avenue.

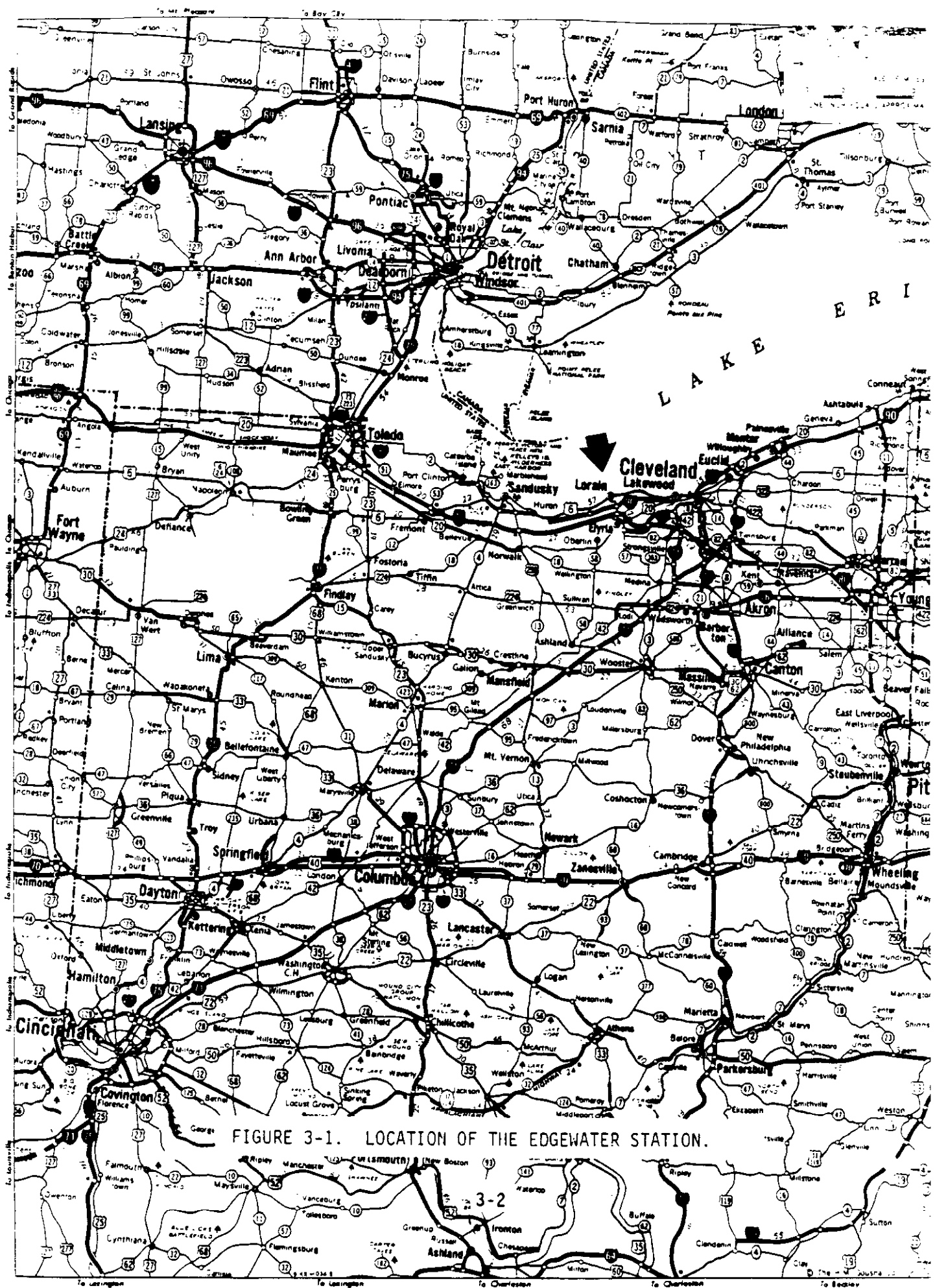


FIGURE 3-1. LOCATION OF THE EDGEWATER STATION.

3-2



Topographically, the site is divided into two fairly level parts by the lakeshore ridge which rises some 20 feet above the lake shore. Approximately two-thirds of the site is located below the ridge and this portion is about six feet above the normal lake level. A plot plan of the site is shown in Figure 3-3. The coal pile and two ash ponds occupy the majority of the lower portion of the site below the power station building. The power station building straddles the ridge. The eastern and the southern sides of the property are contained by a chain link fence.

3.3 EXISTING OFF-SITE FACILITIES

The Edgewater facility is serviced by a road, and access to the site is limited to two entrances, both of which are located on Oberlin Avenue on the east side of the plant. There is no operating rail access to the plant; however, a rail spur does exist. Raw and process water is obtained from the lake through a water intake pipe north of the main building, and cooling water is also drawn from the lake through a cooling water channel which extends from the lake to the power building on the western side of the property.

Solid waste, principally bottom and fly ash, is trucked off-site and disposed of in a company-operated landfill in Sheffield Township, Lorain County, Ohio. This disposal site, a 56-acre tract, has been utilized for 25 years as a solid waste disposal facility. However, a decision as to whether this facility will be used for disposal of LIMB extension solid waste has not been finalized. An alternate site for disposal of the ash is currently being sought by Ohio Edison. In addition, various commercial uses for the LIMB waste are under investigation.

3.4 ENVIRONMENTAL SETTING

The site of the demonstration is an existing coal-fired power station that has been operating since 1919. Very little, if any, natural vegetation exists on the 21-acre site, thus the impacts to the biota will be small. Summary information on the site and surroundings is provided in this section to aid determination of impacts. Much of the information has been taken from two environmental impact statements, one EIS prepared for Lorain Harbor and

1. PLANT OFFICES
2. TRUCK SCALE BUILDING
3. RAIL CAR LOADING AREA
4. YARD OFFICE

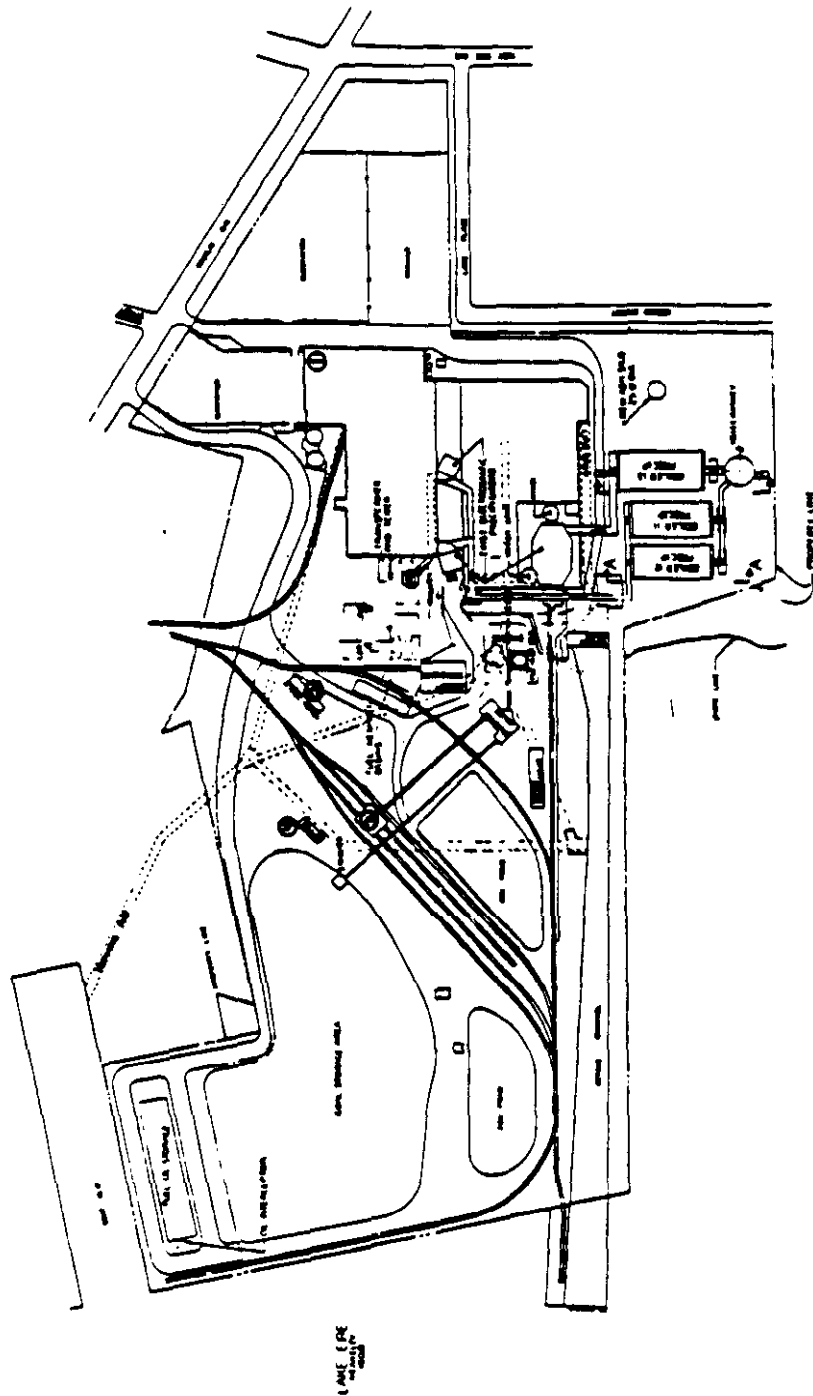


FIGURE 3-3. EDGEWATER PLANT SITE LAYOUT

one for the Lorain Westside facilities plan. The environmental setting of the solid waste disposal area cannot be provided at this time since a site has not been selected.

3.4.1 Local Climate

The region of the site exhibits a humid continental climate, typically an area of interaction between polar and tropical air masses. There are distinctive seasonal changes and the weather is variable. Continental polar air masses from Canada dominate the cold winters. During the summer, as maritime tropical air masses invade the northern latitudes, there is an increase in thunderstorms and precipitation. The temperature is variable over an annual heating cycle and ranges from 0 to 90°F are common. Temperature and precipitation data for the study area are summarized in Table 3-1. Lake Erie near the Edgewater Plant presents an open fetch to the prevailing winds, increasing the importance of mixing by the wind. Figure 3-4 presents a wind diagram for the Beaver Substation, which is located approximately 2.5 miles southwest of the Edgewater facility.

3.4.2 Ambient Air Quality

Ohio Edison Company operated an ambient air quality monitoring network adjacent to the Edgewater facility until 1986. The locations of the four monitoring stations applicable to the Edgewater station are shown in Figure 3-5. The results of monitoring for 1983 through 1985 for SO_x and NO_x are given in Tables 3-2 to 3-7 and their monitoring of TSP for 1983 through 1986 is given in Table 3-8. There have been some exceedences in the primary and secondary 24-hour standards for TSP at monitors adjacent to the station in 1983 and 1984. In particular, the Andorka Lane station showed high values. According to Ohio Edison personnel, this was attributable to fugitive emissions from taconite ore loading operations at the adjacent dock area. This was confirmed by analysis of selected high-volume filters.

3.4.3 Geologic Conditions

The soil association in the area of the station is the Chagrin silt loam association, which is nearly level, moderately well drained, and has a slight erosion potential. The major limitation of the productivity of the soil is seasonal flooding. The soil series is underlain by glacial lake deposits of

TABLE 3-1.

TEMPERATURE AND PRECIPITATION DATA

Month	Temperature			Precipitation					Average Number of Days that have 1.0 inch or more of snow
	Average Daily Maximum °F	Average Daily Minimum °F	Average Highest Maximum °F	Average Lowest Minimum °F	Average Monthly Total In	One year in 10 will have-		Average Monthly Snowfall In	
						Less Than In	More Than In		
January	35.4	19.3	57	-1	2.68	1.11	4.56	9.5	4
February	37.7	20.7	58	0	2.29	1.03	3.76	8.0	3
March	45.1	26.8	69	11	2.94	1.32	4.87	8.8	3
April	59.6	37.4	79	22	3.71	2.05	5.58	1.6	1
May	71.5	47.4	86	32	3.06	1.45	4.93	.1	0
June	80.9	56.3	92	41	3.15	1.46	5.13	0	0
July	84.3	60.3	94	47	2.69	1.14	4.53	0	0
August	82.6	58.6	93	45	3.57	2.01	5.33	0	0
September	77.1	52.6	92	36	2.84	1.28	4.69	0	0
October	66.3	42.2	83	27	2.54	.80	4.73	.4	0
November	51.1	32.6	71	15	2.84	1.20	4.79	4.7	2
December	38.0	22.6	61	1	2.25	1.00	3.74	9.4	4
Year	60.8	39.7	96	-6	34.56	26.21	43.56	42.5	17

NETWORK: EDGEWATER STATION: BEAVER SUB

LEVEL: 10M PERIOD: 1/ 1/85 - 12/31/85

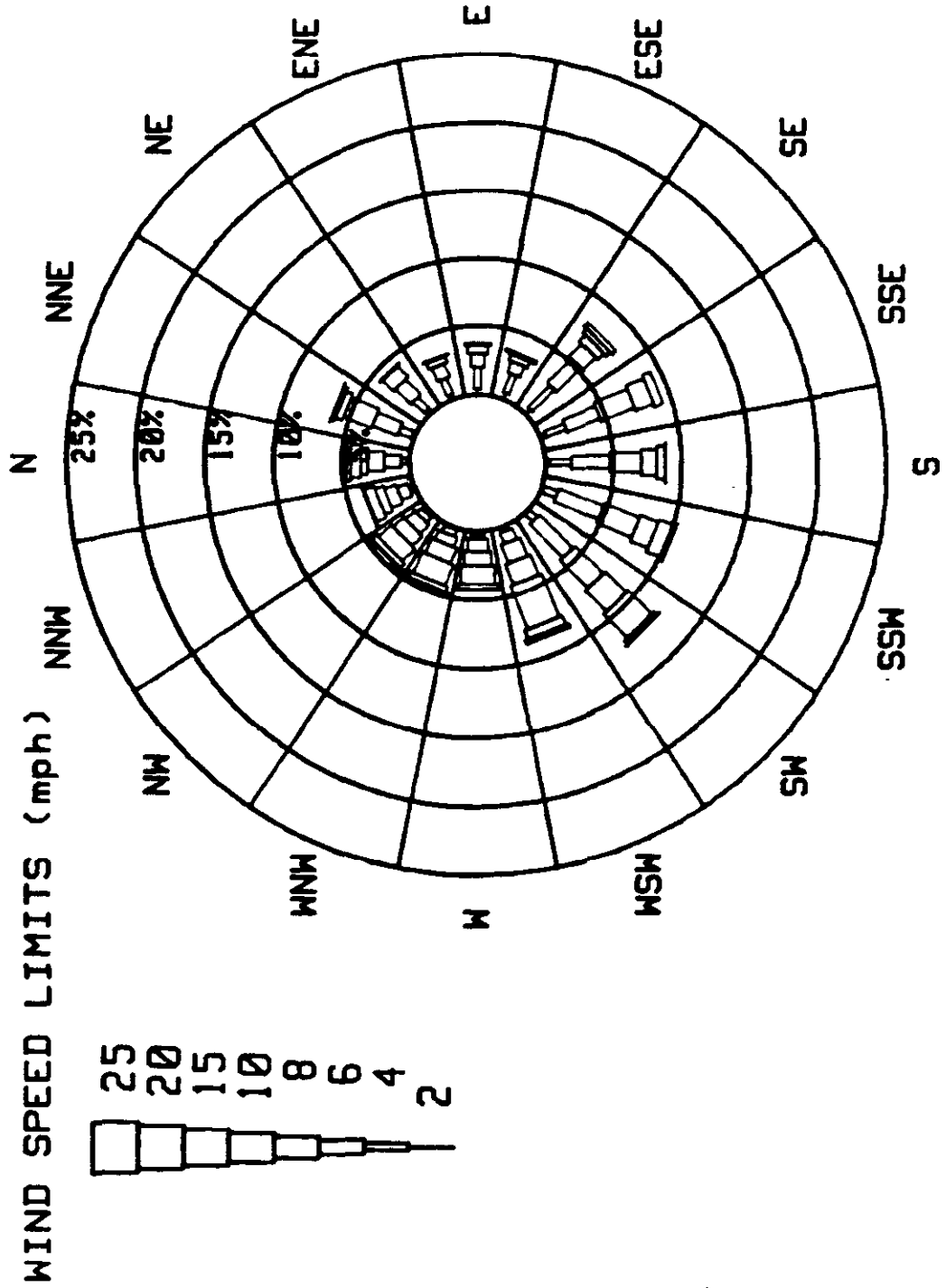


FIGURE 3-4. WIND DIAGRAM FOR BEAVER SUBSTATION.

ESC



FIGURE 3-5. EDGEWATER FACILITY AIR MONITORING NETWORK

TABLE 3-2.

1-, 3- AND 24-HOUR MAXIMUM AND SECOND MAXIMUM
SO₂ CONCENTRATIONS (ppm) for 1983

Station	Maximum 1-Hour Conc. (ppm)	Date : Time	Ann Avg (ppm)
Harrison School	.191	08/24 : 1900	.011
Longfellow Park	.378	04/22 : 1000	.011
Andorka Lanes	.231	08/07 : 1200	.011
Sewage Plant	.329	02/28 : 1600	.014

Station	Maximum 3-Hour Moving Average (ppm)	Date : Time
Harrison School	.122	11/11 : 0600-0800
Longfellow Park	.162	04/22 : 0800-1000
Andorka Lanes	.133	08/07 : 1100-1300
Sewage Plant	.259	02/19 : 1900-2100

Station	2nd Maximum 3-Hour Moving Average (ppm)	Date : Time
Harrison School	.111	07/22 : 1600-1800
Longfellow Park	.157	04/22 : 0900-1100
Andorka Lanes	.128	05/24 : 1000-1200
Sewage Plant	.234	02/28 : 1500-1700

Station	Maximum 24-Hour Moving Average (ppm)	Date : Time
Harrison School	.050	02/10 : 0000 - 02/11: 2300
Longfellow Park	.072	02/10 : 1900 - 02/11: 1800
Andorka Lanes	.060	01/29 : 0000 - 01/30: 2300
Sewage Plant	.123	02/10 : 1600 - 02/11: 1700

Station	2nd Maximum 24-Hour Moving Average (ppm)	Date : Time
Harrison School	.050	02/10 : 0200 - 02/11: 0100
Longfellow Park	.071	02/10 : 1800 - 02/11: 1700
Andorka Lanes	.060	01/29 : 0100 - 01/30: 0000
Sewage Plant	.121	02/10 : 1900 - 02/11: 1800

Station	Maximum 24-Hour Conc ppm	Date	2nd Max 24-Hour Conc ppm	Date
Harrison School	.050	02/10	.041	01/29
Longfellow Park	.059	02/10	.059	01/29
Andorka Lanes	.061	01/29	.054	02/10
Sewage Plant	.107	02/11	.089	11/29

NAAQS: 0.50 ppm (3-hr); 0.14 ppm (24-hr); 0.03 ppm (Annual)

TABLE 3-3.

1-, 3- AND 24-HOUR MAXIMUM AND SECOND MAXIMUM
NO₂ CONCENTRATIONS (ppm) - 1983

Station	Maximum 1-Hour Conc. (ppm)	Date : Time	Ann Avg (ppm)
Longfellow Park	.166	11/09 : 1900	.014
Mt. Carmel Sch	.100	2/13 : 0800	.020
Pleasant Hills	.131	1/23 : 2200	.018
Six	.056	10/31 : 2200	.012

Station	Maximum 3-Hour Moving Average (ppm)	Date : Time
Longfellow Park	.143	11/09 : 1900-2100
Mt. Carmel	.076	11/09 : 1700-1900
Pleasant Hills	.078	2/14 : 0600-0800
Six	.106	1/23 : 2100-2300

Station	2nd Maximum 3-Hour Moving Average (ppm)	Date : Time
Longfellow Park	.131	11/09 : 1800-2000
Mt. Carmel	.074	2/14 : 0700-0900
Pleasant Hills	.078	12/27 : 1000-1200
Six	.100	1/11 : 2000-2200

Station	Maximum 24-Hour Moving Average (ppm)	Date : Time
Longfellow Park	.072	11/09 : 0700 - 11/10: 0600
Mt. Carmel	.063	2/13 : 1400 - 2/14: 1300
Pleasant Hills	.057	2/22 : 0500 - 2/23: 0400
Six	.063	2/13 : 1100 - 2/14: 1000

Station	2nd Maximum 24-Hour Moving Average (ppm)	Date : Time
Longfellow Park	.070	11/09 : 0800 - 11/10: 0700
Mt. Carmel	.062	2/13 : 1300 - 2/14: 1200
Pleasant Hills	.057	2/22 : 0600 - 2/23: 0500
Six	.062	2/13 : 1200 - 2/14: 1300

Station	Maximum 24-Hour Conc ppm	Date	2nd Max 24-Hour Conc ppm	Date
Longfellow Park	.046	7/14	.041	7/ 8
Mt. Carmel	.058	2/14	.052	2/13
Pleasant Hills	.055	3/ 4	.053	2/15
Six	.062	2/28	.060	2/22

NAAQS: 0.050 ppm (Annual); Proposed - 0.250 ppm (1-hr

TABLE 3-4.

1-, 3- AND 24-HOUR MAXIMUM AND SECOND MAXIMUM
SO₂ CONCENTRATIONS (ppm) for 1984

Station	Maximum 1-Hour Conc. (ppm)	Date : Time	Ann Avg (ppm)
Harrison School	.241	6/22 : 1600	.008
Longfellow Park	.292	5/31 : 0900	.011
Andorka Lanes	.211	1/26 : 0400	.007
Sewage Plant	.263	7/13 : 0200	.011

Station	Maximum 3-hour Moving Average (ppm)	Date : Time
Harrison School	.203	6/22 : 1500-1700
Longfellow Park	.203	5/31 : 0800-1000
Andorka Lanes	.177	6/22 : 1500-1700
Sewage Plant	.213	6/18 : 0500-0700

Station	2nd Maximum 3-Hour Moving Average (ppm)	Date : Time
Harrison School	.184	6/22 : 1400-1600
Longfellow Park	.192	4/09 : 1600-1800
Andorka Lanes	.172	6/22 : 1600-1800
Sewage Plant	.199	3/22 : 0800-1000

Station	Maximum 24-Hour Moving Average (ppm)	Date : Time
Harrison School	.061	6/21 : 1900 - 6/22 : 1800
Longfellow Park	.080	5/30 : 2300 - 5/31 : 2200
Andorka Lanes	.060	3/15 : 0100 - 3/16 : 0000
Sewage Plant	.064	6/17 : 2000 - 6/18 : 1900

Station	2nd Maximum 24-Hour Moving Average (ppm)	Date : Time
Harrison School	.061	6/21 : 2000 - 6/22 : 1900
Longfellow Park	.080	5/31 : 0000 - 5/31 : 2300
Andorka Lanes	.059	3/15 : 0200 - 3/16 : 0100
Sewage Plant	.064	6/17 : 2100 - 6/18 : 2000

Station	Maximum 24-Hour Conc. (ppm)	Date	2nd Max 24-Hour Conc. (ppm)	Date
Harrison School	.053	10/13	.046	6/22
Longfellow Park	.081	5/31	.067	5/27
Andorka Lanes	.058	3/15	.058	10/15
Sewage Plant	.065	6/18	.065	10/13

NAAQS: 0.50 ppm (3-hr); 0.14 ppm (24-hr); 0.03 ppm (Annual)

TABLE 3-5.

1-, 3- AND 24-HOUR MAXIMUM AND SECOND MAXIMUM
NO₂ CONCENTRATIONS (ppm) for 1984

Station	Maximum 1-Hour Conc. (ppm)	Date : Time	Ann Avg (ppm)	
Longfellow Park	.126	3/24 : 0400	.016	
Pleasant Hills	.065	6/05 : 0200	.013	
Six	.074	6/10 : 2200	.012	
Crow	.068	8/13 : 0000	.013	
Maximum 3-Hour Moving Average				
Station	(ppm)	Date : Time		
Longfellow Park	.111	3/24 : 0300-0500		
Pleasant Hills	.058	6/05 : 0200-0400		
Six	.066	1/12 : 1900-2100		
Crow	.060	4/26 : 1300-1500		
2nd Maximum 3-Hour Moving Average				
Station	(ppm)	Date : Time		
Longfellow Park	.103	3/24 : 0400-0600		
Pleasant Hills	.055	6/05 : 0300-0500		
Six	.063	6/05 : 0300-0500		
Crow	.057	8/21 : 1300-1500		
Maximum 24-Hour Moving Average				
Station	(ppm)	Date : Time		
Longfellow Park	.056	5/30 : 2300 - 5/31 : 2200		
Pleasant Hills	.040	2/23 : 0500 - 2/24 : 0400		
Six	.042	2/22 : 2300 - 2/23 : 2200		
Crow	.029	2/23 : 1400 - 2/24 : 1300		
2nd Maximum 24-Hour Moving Average				
Station	(ppm)	Date : Time		
Longfellow Park	.056	5/31 : 0000 - 5/31 : 2300		
Pleasant Hills	.040	2/23 : 0600 - 2/24 : 0500		
Six	.042	2/23 : 0000 - 2/23 : 2300		
Crow	.028	2/23 : 1500 - 2/24 : 1400		
Maximum 24-Hour Conc.				
Station	(ppm)	Date	2nd Max 24-Hour Conc. (ppm)	Date
Longfellow Park	.055	5/31	.040	6/01
Pleasant Hills	.038	2/23	.035	11/25
Six	.042	2/23	.039	11/25
Crow	.028	11/24	.027	6/22

NAAS: 0.05 ppm (Annual); Proposed 0.25 ppm (1-hr)

TABLE 3-6.

1-, 3- AND 24-HOUR MAXIMUM AND SECOND MAXIMUM
SO₂ CONCENTRATIONS (ppm) for 1985

Station	Maximum 1-Hour Conc. (ppm)	Date : Time	Ann Avg (ppm)
Harrison School	.227	5/23 : 1700	.007
Longfellow Park	.186	1/16 : 2200	.007
Andorka Lanes	.206	1/16 : 2200	.009
Sewage Plant	.314	3/31 : 2200	.012

Station	Maximum 3-Hour Moving Average (ppm)	Date : Time
Harrison School	.160	5/23 : 1700-1900
Longfellow Park	.116	1/16 : 2000-2200
Andorka Lanes	.149	5/23 : 1700-1900
Sewage Plant	.268	1/21 : 1800-2000

Station	2nd Maximum 3-Hour Moving Average (ppm)	Date : Time
Harrison School	.135	5/29 : 1600-1800
Longfellow Park	.110	5/28 : 1700-1900
Andorka Lanes	.124	1/16 : 2000-2200
Sewage Plant	.257	1/21 : 1700-1900

Station	Maximum 24-Hour Moving Average (ppm)	Date : Time
Harrison School	.036	5/29 : 0300 - 5/30 : 0200
Longfellow Park	.060	1/30 : 1900 - 1/31 : 1800
Andorka Lanes	.059	1/30 : 2000 - 1/31 : 1900
Sewage Plant	.148	1/20 : 2100 - 1/21 : 2000

Station	2nd Maximum 24-Hour Moving Average (ppm)	Date : Time
Harrison School	.036	5/29 : 0500 - 5/30 : 0400
Longfellow Park	.060	1/30 : 2000 - 1/31 : 1900
Andorka Lanes	.058	1/30 : 1900 - 1/31 : 1800
Sewage Plant	.147	1/20 : 2200 - 1/21 : 2100

Station	Maximum 24-Hour Conc. (ppm)	Date	2nd Max 24-Hour Conc. (ppm)	Date
Harrison School	.035	5/23	.031	10/30
Longfellow Park	.058	1/31	.046	2/11
Andorka Lanes	.055	1/31	.053	2/11
Sewage Plant	.145	1/21	.087	2/14

NAAQS: 0.50 ppm (3-hr); 0.14 ppm (24-hr); 0.03 ppm (Annual)

TABLE 3-7.

1-, 3- AND 24-HOUR MAXIMUM AND SECOND MAXIMUM
NO₂ CONCENTRATIONS (ppm) for 1985

	Maximum 1-Hour Conc.			Ann Avg
Station	(ppm)	Date : Time		(ppm)
Longfellow Park	.075	6/08 : 0000		.016
Pleasant Hills	.075	2/10 : 2200		.013
Six	.082	2/04 : 0600		.011
Crow	.067	4/27 : 1400		.012
Station	Maximum 3-Hour Moving Average			
	(ppm)	Date : Time		
Longfellow Park	.065	2/20 : 1800-2000		
Pleasant Hills	.060	2/10 : 2000-2200		
Six	.079	2/04 : 0500-0700		
Crow	.061	4/27 : 1400-1600		
Station	2nd Maximum 3-Hour Moving Average			
	(ppm)	Date : Time		
Longfellow Park	.064	5/01 : 0000-0200		
Pleasant Hills	.058	2/11 : 0000-0200		
Six	.074	2/04 : 0600-0800		
Crow	.054	4/27 : 1300-1500		
Station	Maximum 24-Hour Moving Average			
	(ppm)	Date : Time		
Longfellow Park	.047	2/05 : 0500 - 2/06 : 0400		
Pleasant Hills	.045	2/10 : 1700 - 2/11 : 1600		
Six	.046	2/04 : 0400 - 2/05 : 0300		
Crow	.034	2/04 : 0400 - 2/05 : 0300		
Station	2nd Maximum 24-Hour Moving Average			
	(ppm)	Date : Time		
Longfellow Park	.047	2/05 : 0600 - 2/06 : 0500		
Pleasant Hills	.044	2/10 : 1600 - 2/11 : 1500		
Six	.046	2/04 : 0500 - 2/05 : 0400		
Crow	.034	2/04 : 0500 - 2/05 : 0400		
Station	Maximum 24-Hour Conc.		2nd Max 24-Hour Conc.	
	(ppm)	Date	(ppm)	Date
Longfellow Park	.044	2/11	.041	4/04
Pleasant Hills	.037	2/11	.033	12/20
Six	.045	2/04	.042	2/11
Crow	.032	2/04	.030	2/01

NAAQS: 0.05 ppm (Annual); Proposed 0.25 ppm (1-hr)

TABLE 3-8. SUMMARY OF 24-HOUR TSP/IP CONCENTRATIONS
(ugms/m³; 1983 through 1986)

Site	Type	Max.	Date	2nd Max.	Date	Geo. Mean	Std. Dev.
Harrison School	PRI	146	3/83	115	6/83	53.6	1.5
	IP	38	3/83	88	9/83	37.8	1.6
Longfellow Park	PRI	173	9/83	150	8/83	52.0	1.7
Andorka Lanes	PRI	319	10/83	257	8/83	80.8	1.9
	SEC	293	10/83	247	6/83	76.4	1.8
	IP	192	10/83	150	8/83	47.7	1.9
Sewage Plant	PRI	232	11/83	147	10/83	55.6	1.7
Harrison School	PRI	166	4/84	136	4/84	45.3	1.6
	IP	106	4/84	82	10/84	32.6	1.7
Longfellow Park	PRI	180	4/84	150	11/84	47.4	1.8
Andorka Lanes	PRI	386	11/84	313	6/84	64.9	1.9
	SEC	484	11/84	320	6/84	69.0	1.9
	IP	268	11/84	186	6/84	40.5	2.0
Sewage Plant	PRI	200	6/84	181	8/84	52.9	1.9
Harrison School	PRI	221	5/85	90	4/85	35.3	1.8
	IP	122	5/85	63	1/85	24.3	1.8
Longfellow Park	PRI	240	5/85	120	9/85	41.0	1.9
Andorka Lanes	PRI	215	5/85	202	7/85	59.1	2.2
	SEC	278	5/85	211	5/85	56.3	2.1
	IP	165	5/85	125	5/85	33.7	2.2
Sewage Plant	PRI	225	5/85	166	4/85	40.6	2.0
Harrison School	IP	110	4/86	80	7/86	63.2	--
	PRI	75	4/86	73	7/86	44.2	--
Longfellow Park	IP	111	7/86	86	5/86	71.7	--
Andorka Lanes	IP	285	7/86	112	5/86	94.5	--
	PRI	120	7/86	78	8/86	61.2	--
Sewage Plant	IP	99	7/86	94	4/86	67.6	--

PRI = Primary
SEC = Secondary
IP = Inhalable Particulate

the Wisconsin age, which consists of laminated silts and clays (5 to 50 feet thick) underlain by till. The underlying bedrock is composed of the Olentangy and Ohio shales. No faulting was discerned in the vicinity.

Seismicity is negligible; significant earthquakes in Ohio are infrequent. Within a 40 mile radius of the plant, the only recorded earthquakes were II-V on the Modified Mercalli intensity scale (MMI). Only one earthquake was recorded in Lorain County--a IV-VI on the MMI in 1928. In addition, there was a mild earthquake at N.E. Ohio in January, 1986.

At the Edgewater facility, erosion potential and topographic instability do not present problems. The area is reinforced and protected by a steel bulkhead. However, the coal storage pile, the ash ponds, the limestone silo and new compressor are on the 100-year floodplain approximately six feet above the mean lake level.

3.4.4 Ecological Conditions

The Edgewater site has very little value as habitat for wildlife because of its previous and existing use as a coal-fired power station. Two environmental impact statements for the projects conducted adjacent to the Edgewater facility were reviewed to determine the potential presence of unique ecological or sensitive communities in surrounding areas. Following is a quote from the Lorain Harbor EIS.

The Lorain Harbor area was inspected by a biologist of the USF&WS, and it was determined that no suitable habitat for endangered species exists. However, the project does lie within the range of the Indiana bat (Myotis sodalis) which is a federally endangered species. Coordination with ODNR's Natural Heritage Program has revealed that the silver lamprey (Ichthyomyzon unicuspis), a state endangered species, was collected in the Black River approximately 3,000 feet upstream near the AmShip drydocks.

According to USF&WS, a moderately diverse fish community persists in Lorain Harbor in spite of rather limited physical habitat and degraded water quality. Within the past ten years, 47 species of fish have been identified for the Outer Harbor. During the same period of time, 41 species of fish have been collected within the lower reaches of the Black River. Gizzard shad and emerald shiner dominate the catches in both the Outer Harbor and the lower river area. Freshwater drum, smelt, white bass, spot-tail shiner, trout perch and yellow perch are also common in the Outer Harbor. Trout perch are also very common in the lower river along with carp, brown bullhead and white sucker. Spawning and nursery habitat for fish are almost nonexistent in the lower river area and in

the Outer Harbor. The habitat is severely limited because of deep navigation channels.

Lorain Harbor is located on the eastern edge of the Mississippi flyway and on the western edge of the Atlantic flyway, thus attracting large numbers of ducks, geese and swan, which pass through the area on migratory flights between southern wintering grounds and northern breeding grounds. The Outer Harbor provides good feeding habitat for many species of diving ducks including mergansers and scaup. The only abundant dabbling duck is the mallard. Herring gulls, ring-billed gulls and Bonaparte gulls are also attracted to the Outer Harbor. No significant amounts of waterfowl breeding occur in either the Outer Harbor or the lower reaches of the Black River.

Figure 3-6 shows the relative location of the Lorain Harbor to the Edgewater Station. The ecological conditions surrounding the proposed off-site disposal facility cannot be discussed until the disposal site has been selected.

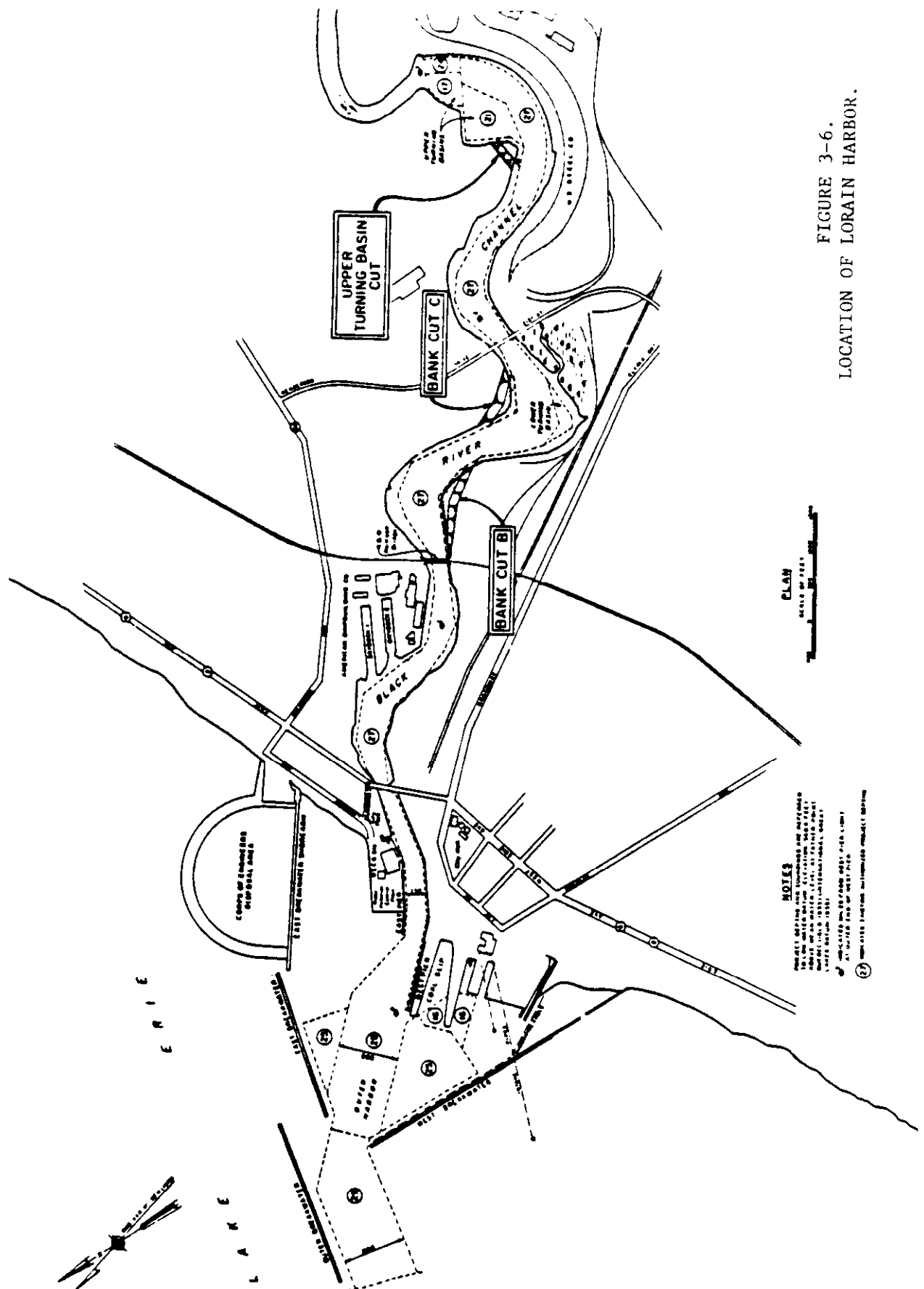
3.4.5 Socioeconomic Conditions

The population of Lorain County in 1980 was 274,909 up from 256,843 in 1970. The population of the city of Lorain in 1980 was 75,416 down from 78,185 in 1970. The average unemployment rate in 1981 for Lorain County was 13.3 percent. Lorain County unemployment in 1984 exceeded 20 percent. Manufacturing plays a major role in Lorain's economy. In 1978 40,997 people, or 38.6 percent of the labor force were employed by 55 diversified manufacturing industries in the area. The principal industries in the Lorain area include steel, shipbuilding and automobiles.

Lorain County, Ohio, is characterized by high unemployment due to depressed economic conditions which have severely impacted American Shipbuilding and U. S. Steel, major employers in the areas. A protracted decline in the construction industry, particularly related to shipbuilding and steel production, has resulted in an overabundance of unemployed skilled craft workers.

3.4.6 Aesthetic Conditions

The area in the vicinity of the proposed demonstration plant is heavily industrialized. Examples of adjacent operations include a USX steel making plant which is currently shut down. As such, there are no especially scenic vistas in this general area.



There should not be any impacts to sites either listed in or eligible for the National Register of Historic Places, since the LIMB and Coolside demonstrations will be built on an already disturbed site. There are a number of individual properties in Lorain which are listed in the National Register of Historic Places. Only the Lorain Lighthouse, located on the west breakwater, is within the study area. There are no historic properties or archeological sites that have been identified on the proposed site of the LIMB Extension Demonstration Project.

No information can be provided on the proposed ash disposal site since the site has not yet been selected.

3.4.7 Tribal or Religious Practices

Babcock and Wilcox is not aware of any unique ethnic, tribal or religious practices that are indigenous to the site vicinity which could be affected by the demonstration project.

3.4.8 Identification of Any Other Planned Major Energy or Chemical Complexes

Babcock and Wilcox is presently unaware of any plans for the construction of additional major energy and chemical complexes in the vicinity of the proposed project. As previously discussed, the area is heavily industrialized and areas to the south of the facility are residential. There is little, if any, vacant land available for construction of major energy or chemical complexes.

4.0 PROJECT DESCRIPTION

4.1 INTRODUCTION

This project, entitled the LIMB Demonstration Project Extension, is an extension to an existing project with the U. S. EPA, currently being constructed at the Edgewater station of Ohio Edison.

The purpose of the original EPA project was to identify LIMB as a viable retrofit technology for reducing both sulfur dioxide and nitrous oxide emissions from utility power generation plants. In addition, an extension technology termed Coolside is to be demonstrated as a viable method for reducing sulfur dioxide by injecting sorbent into the flue gas ductwork after the boiler. LIMB and Coolside as retrofit technologies would be more economical than the major alternative, wet flue gas scrubbers. Successful application of the technology to an existing boiler is expected to demonstrate that 1) significant reduction of SO_x and NO_x emissions can be achieved at a fraction of the cost of add-on wet flue gas desulfurization systems; 2) boiler reliability, operability and steam production can be maintained at levels existing prior to retrofit of the LIMB system; and 3) technical difficulties attributable to LIMB operations such as additional slagging and fouling, changes in the ash disposal requirements and an increased particulate load can be resolved in a cost-effective manner. Additional utility requirements over the EPA LIMB project are negligible since humidification will be operational under the original EPA project.

The following sections present a brief description of the technology, discuss resource requirements and describe the project in relation to the overall plant setting.

4.1.1 The LIMB Process

The LIMB process is being designed in detail for Ohio Edison's Edgewater Unit No. 4, Boiler No. 13, for the LIMB demonstration which Babcock and Wilcox is conducting for the U. S. EPA under Contract No. 68-02-4000 (see Table 4-1 for pertinent data on the unit). This design is directly applicable to

TABLE 4-1. HOST SITE BOILER

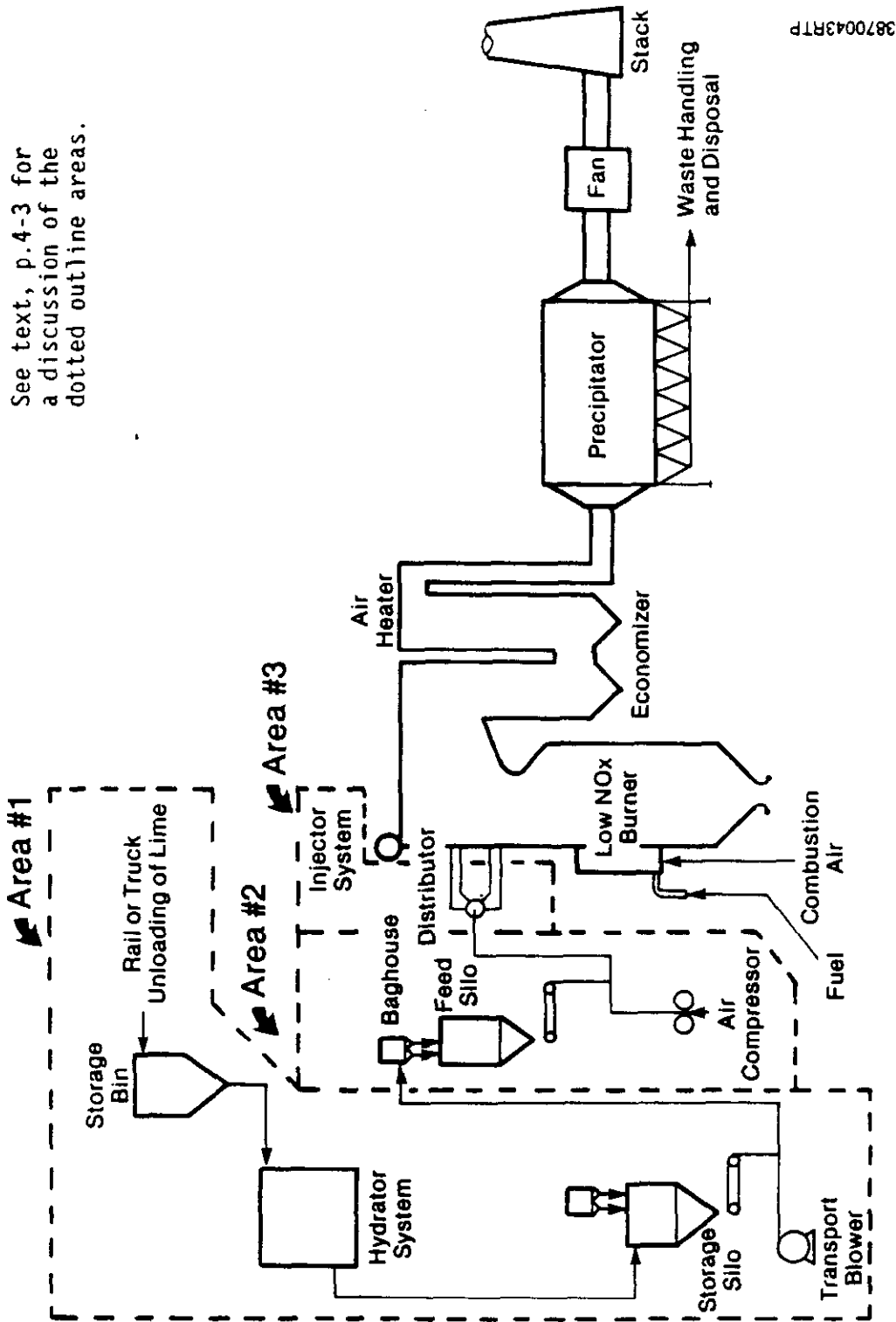
-
1. UTILITY: Ohio Edison Company
 2. UNIT ID: Edgewater No. 4
 3. LOCATION: 200 Oberlin Avenue, Lorain, Lorain County, Ohio 44052
 4. NAME PLATE RATE: 105 MWe
 5. TYPE: Steam Turbine
 6. PRIMARY FUEL: Eastern Bituminous Coal
 7. ALTERNATE FUEL: None
 8. STATUS: Existing
 9. OPERATION DATE: June 1, 1957
 10. BOILER ID: No. 13 (B&W RB-231)
 11. BOILER GENERAL CONDITION: Excellent
 12. BOILER MANUFACTURER: Babcock & Wilcox
 13. BOILER TYPE: Radiant, Wall-Fired, Carolina Design
 14. STEAM FLOW: 690,000 lb/hr
 15. SH OUTLET PRESSURE: 1480 psig
 16. STEAM TEMPERATURES: 1000F SH/1000F RH
 17. DESIGN PRESSURE: 1650 psig
 18. DEMONSTRATION FUEL: Ohio Bituminous, 1.5%, 3% and 3.8% sulfur
 19. BURNERS: Original circular have been replaced with low-NO_x burners
 20. PARTICULATE CONTROL: Lodge-Cottrell ESP, 3 years old,
conservatively designed.
 21. SORBENT STORAGE & HANDLING SPACE: 150' x 120' = 18,000 ft²
available
 22. BOILER AVAILABILITY: 90% (currently) using 1.5 Sulfur Coal;
available for the LIMB demonstration as
on the dispatch schedule.
 23. PAST EMISSION MONITORING: Opacity - Certified
SO₂ and CO₂ - Certifiable
 24. BOILER DESIGN:
Furnace Volume - 52,300 ft³
Heat Release Rate - 11,000 Btu/lb x 84,900 lb/hr = 9.34 x 10⁸ Btu/hr
Gas Temperatures - Lvg. Econ. 605^oF; Lvg Air Heater 275^oF
Installed Instrumentation
Convective Pass Design - Pendant SSH & RH; Horizontal PSH & Econ.;
Tubular Air Heater
Slagging/Fouling History - No major problems
Sootblowing Capacity - (2) Joys @ 1150 CFM, 300 psig each;
total 2300 CFM
Coal Mill Capacity - (4) Mills 13-14 tons/hr each
Load Dispatch Priority - May 1984: 23 using 1.5% Sulfur Coal
-

utility boilers being considered for SO_x/NO_x abatement retrofit technology. The same process and equipment will be used in the DOE LIMB Demonstration Project Extension.

The LIMB injection system consists of three subsystems to provide sorbent injection into the boiler. These are 1) the sorbent handling and preparation system, 2) the feed system, and 3) the distribution system. (See Figure 4-1.) The sorbent storage and handling system is responsible for supplying and preparing sorbent for the process. The sorbent will be delivered by bulk transport truck. It is dry and pulverized material suitable for pneumatic conveying. The sorbent is stored in a bin or silo from which it can be fed to the sorbent delivery system and pneumatically injected into the boiler. The objective of the sorbent feed system is to provide a controlled feed rate of sorbent to the injection elevations in the boiler. This system is duplicated for each injection elevation. Material is conveyed in dense phase from the feed silo bottom to a vertical pickup station from which it is conveyed in dilute phase to a distributor bottle. Each bottle distributes the solids and air mixture into the injection lines. Air used in transport of the sorbent would be supplied by a compressor and dried with an air dryer. At the boiler the distribution system will be provided to give the desired penetration and dispersion of sorbent into the boiler. A booster air fan will be needed to provide the air necessary for the desired penetration and dispersion.

Additional soot blowers will be required to deal with the effects of higher solids concentration in the furnace gases as a result of sorbent injection.

If the increased solids loading in the flue gas entering the electrostatic precipitator causes degradation of performance, performance can be improved by pretreatment of the flue gas prior to entering the ESP. This pretreatment will consist of humidification and cooling which will increase residence time in that unit and improve electrical conductivity in the gas solids mixture. This will improve the particles' susceptibility to collection. The primary goals of humidification are improved SO_2 removal and increased precipitator efficiency.



3870043RTP

Figure 4-1. LIMB Demonstration Issues

See text, p.4-3 for a discussion of the dotted outline areas.

To meet the NO_x emissions reduction goal of LIMB, low- NO_x pulverized coal burners are required as retrofit. Babcock and Wilcox-developed dual register and XCL low- NO_x burners are generally compatible with utility boilers and should be easily retrofitted to the operating unit. For LIMB, the XCL low- NO_x burners have been installed at the Edgewater station. Under the LIMB Extension Demonstration, the range of applicability of the LIMB process will be demonstrated on a range of coal sulfur contents. No hardware changes will be made; however, sorbent ratios will be adjusted.

4.1.2 The Conoco Coolside Process

The Coolside process involves hydrated lime injection, flue gas humidification and additive injection into the ductwork downstream of the air preheater. (See Figure 4-2.) The Coolside process will use the same sorbent storage silo as the LIMB process. The sorbent is pneumatically conveyed and injected into the flue gas duct downstream of the boiler air preheater.

A water-soluble additive can be injected into the humidifier in solution with the humidification water to enhance the process SO_2 removal. The additive being considered for the demonstration will be sodium hydroxide, the same additive used in Conoco's 1 MW field test. Work will be carried out to select the additive and to characterize the properties of simulated Edgewater Coolside waste to be disposed of. The spent sorbent is removed along with coal fly ash as a dry solid waste in the ESP. A portion of the ESP solids can be recycled to reduce the fresh lime requirement if the particulate collection system can handle the solids loading resulting from recycle. In this demonstration, both once-through and sorbent recycle will be evaluated. The ESP at the host site is large enough to demonstrate sorbent recycle. Commercial hydrated lime will be delivered to the test site instead of on-site hydration of calcined lime.

The Coolside process demonstration will use full-scale commercial equipment for all the process components. These components include the hydrated lime feed system, the flue gas humidification system, additive injection system and the existing ESP. In addition, a sorbent recycle system will be installed to allow a portion of the ESP waste solids to be reinjected along with the fresh lime into the Coolside duct.

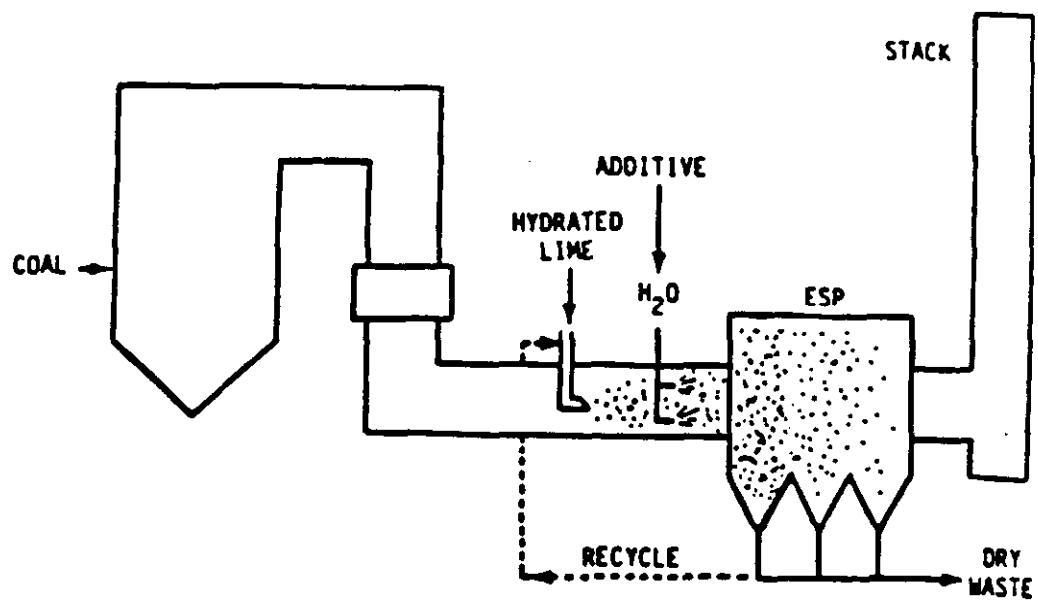


FIGURE 4-2. COOLSIDE HYDRATED LIME INJECTION

4.2 PROJECT RESOURCE REQUIREMENTS

Since Edgewater is the host site for the EPA LIMB demonstration, most of the process equipment which is required for the DOE Coolside demonstration is already in place. The EPA LIMB and humidification demonstrations will have installed 90 percent of the equipment needed for Coolside, minimizing the capital and labor costs of Coolside. Since the required utilities are in place and arrangements will have been made for solid waste disposal for the LIMB, these costs will be minimal at the Ohio Edison site.

In addition to project costs, the time for manpower training will be minimal since the majority of the operators will have worked on the EPA-sponsored projects. The manpower experience factor should lead to a safe operation.

4.3 RAW MATERIALS AND UTILITY REQUIREMENTS

The raw material and utility requirements for the LIMB and Coolside are summarized in Table 4-2. Raw materials required for the LIMB extension are various coals and sorbents. Three different coal sulfur levels will be tested in the extension program, 1.5 percent, 3 percent, and 3.8 percent sulfur. Approximately 60,000 tons of each coal will be required to perform the desired test program. Each coal will be purchased through Ohio Edison, the host utility, delivered to, stockpiled on and managed at the existing coal storage property.

Demonstration of the Coolside technology which is scheduled to occur prior to the DOE LIMB testing will utilize the 3.0 percent sulfur coal and hydrated calcitic lime as raw materials. Approximately 60,000 tons of coal and a maximum of 6,000 tons of sorbent will be necessary for the testing program. One raw material required for the Coolside demonstration will be 50 percent sodium hydroxide solution, which is the additive which helps promote SO_2 removal. This solution will be delivered by tanker truck (24,500 gallons per week, maximum) and stored in the plant's existing caustic tank at the facility. Quantities of sulfuric acid will also be purchased to be used to maintain effluent pH in the regulated range. The exact quantities of sulfuric acid that will be purchased are not known at this time.

TABLE 4-2. RAW MATERIALS AND UTILITY REQUIREMENTS

Material/ Utility	Station Requirements w/o Project	LIMB/ LIMB Extension	Coolside includes humidification
Coal	160,000 TPY	180,000 TPY	60,000 Tons
Sorbent	0 TPY	9,000 T calcitic limestone 16,000 T dolomitic limestone 8,000 T dolomitic hydrated lime 2,500 T promoted lime	6,000 Tons
Acid for pH Control	0	Unknown	Unknown
Additive NaOH for Conditioning		0	1,200 Tons of 50% solution
Water			
- Cooling	110 MGD	.03 MGD	.36 MGD
- Process	1.14 MGD	.14 MGD	.12 MGD
Operating Labor		0 additional	0 additional
Construction Labor	0	<-----30-50 people----->	
Power		440 hp	1,340 hp

The EPA LIMB project utilizes calcitic hydrated lime as the sorbent. A total of four additional sorbents will be tried in the DOE project. These will be chosen from a list of sorbents, including calcitic limestone, dolomitic limestone, dolomitic hydrated lime and a promoted lime which is yet to be identified. For the purposes of the proposed DOE LIMB project the following approximate requirements for each possible sorbent are anticipated: calcitic limestone, 9,000 tons; dolomitic limestone, 16,000 tons; dolomitic hydrated lime, 8,000 tons; and promoted lime, 2,500 tons.

The quantities of each sorbent required will be delivered to the plant by self-unloading bulk transport trucks which will fill the sorbent storage and handling systems. For the DOE LIMB project, 10-12 truckloads of additive will be delivered to the station every weekday, during the day shift. The Coolside demonstration will require eight trucks of sorbent a day. Additional coal trucks will be required on a short term basis to increase the inventory, but impacts will be minimal.

The added utility requirements for the DOE LIMB Demonstration Project Extension are primarily electrical in nature. However, the additional operating requirements have not yet been estimated. Additional electrical equipment over and above normal plant needs without LIMB includes the sorbent feed pump compressor, the conveying air compressor, booster air blowers and various other pumps and fans. In addition, several air heaters will be needed to preheat ash transport air. It is estimated that an additional 440 installed horsepower is required for the LIMB system. Coolside, with the sorbent recycle, will require 1,340 additional installed horsepower to drive the humidification atomization air compressor, humidification water and raw water pumps. Another recycle transport blower and booster air blower may also be needed. Some additional steam will be needed for the extra boiler soot blowers that will be installed to prevent tube fouling. This demand of steam will be intermittent and will be small compared with the amount of steam available at the power plant. In addition, a significant amount of steam will be required for flue gas reheating to prevent localized condensation from flue gas at low approach to saturation conditions.

The land requirements to construct the project are also small since it is a retrofit project. No additional land will be purchased by Ohio Edison. All equipment will be located within existing fence lines. Additional space requirements for the LIMB project at the host site include space for a new unpaved roadway around the new sorbent storage silo. The roadway will be approximately 200 feet long and 30 feet wide. The Coolside work will require a compressor and recycle sorbent storage silo pad.

The land requirements for waste disposal are potentially significant. The LIMB portion of the project will generate up to 12.5 tph of waste including slaking water and the Coolside portion of the project up to 11.6 tph. Of this waste, 72-76 percent is a result of the spent sorbent and 26-28 percent is flyash which would be generated without the project. The EPA LIMB work is projected to last 12 months, DOE LIMB work, 14 months and the DOE Coolside activities 4 months. Using a 43 percent capacity utilization factor and assuming 2,200 tons will occupy 1 acre-foot, the DOE LIMB work will generate 22 acre-feet of wastes including flyash and the DOE Coolside portion of the project will generate 10 acre-feet including flyash. Assuming a 10-foot fill depth, approximately 3 acres of land will be needed over the life of the DOE LIMB Demonstration Project Extension. A large portion of this waste would otherwise exhaust from the boiler stack as fly ash, SO_x and NO_x . A landfill for the project solid waste has not been selected at this time.

Peak project labor requirements for the construction of the DOE LIMB Demonstration Project Extension should place no undue stress on the existing area labor resources since the area is characterized by high unemployment among skilled craftsmen due to depressed economic conditions. The labor requirements during operation will be much less. No additional permanent power plant staff are anticipated for operating either the LIMB or Coolside Systems. However, additional B&W, Conoco and Radian personnel will be on-site only for the duration of the project.

For the proposed technology, manufacturing of equipment is easily performed due to the large overcapacity within the industry. In addition, there are no unusual fabrication requirements that would preclude the use of existing manufacturing facilities. The nature of the individual components

make LIMB and Coolside technologies very compatible with existing power plant and environmental manufacturing methods. The water requirements of the project are discussed in later sections.

4.4 PROJECT SITE PLAN

4.4.1 Description of Physical Appearance

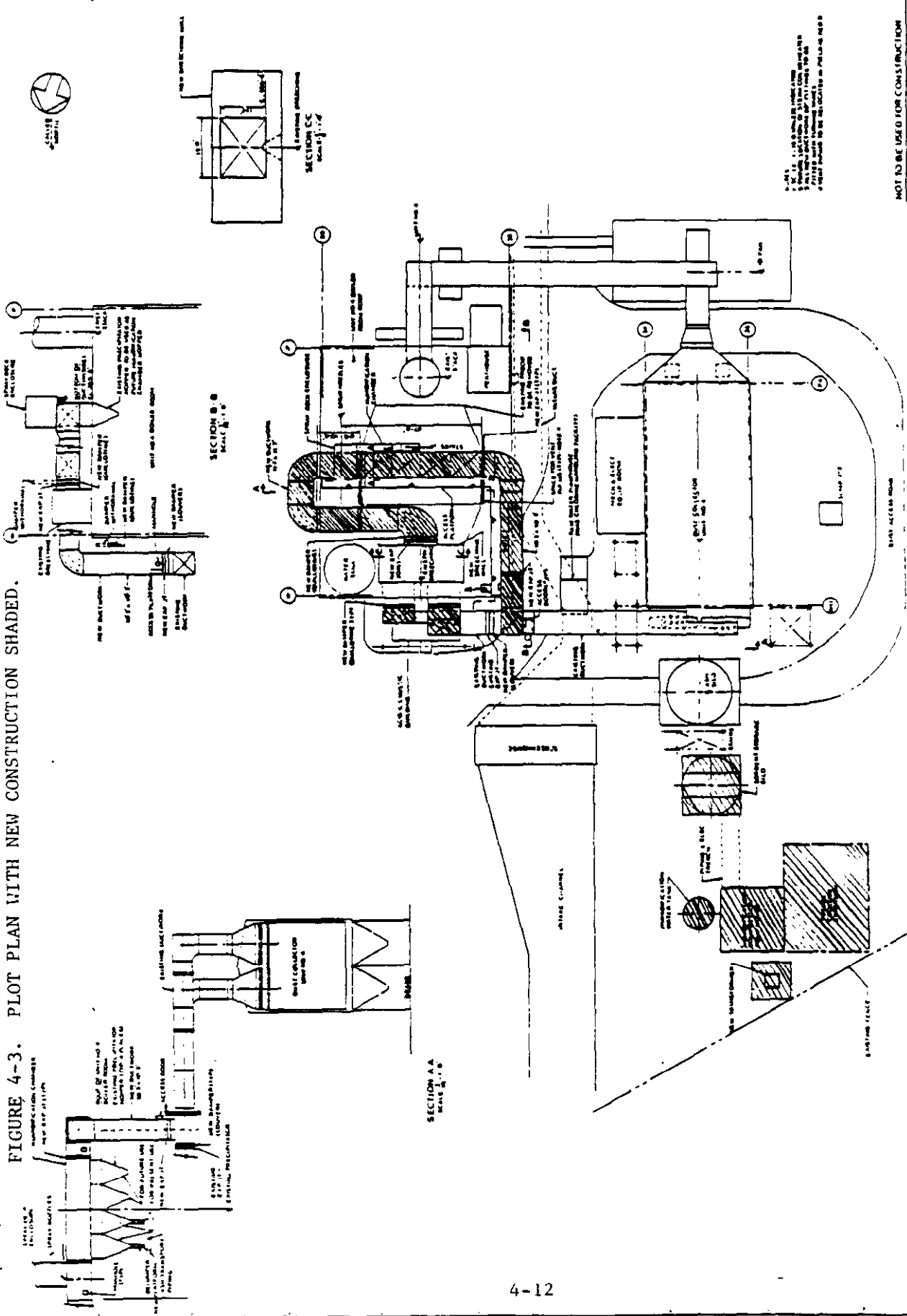
The LIMB Demonstration Project Extension is to be conducted on the Edgewater Unit No. 4. The demonstration will include provisions for additional equipment adjacent to Unit No. 4 boiler and its associated control equipment. This boiler is located on the northeast corner of the plant. A specific plot plan of the area affected by the project is given in Figure 4-3. The majority of the modifications will be made to existing equipment and will consist of very little new construction. The humidification portion of the Coolside project will require an additional compressor located inside the boiler house, provisions for ash recycle and provision of a bypass duct.

There will be very little change in the physical appearance of the facility with the exception of the new sorbent silo and modified or additional inlet ductwork to the ESP. These modifications will probably not be noticeable from the outside of the plant since the changes are made on the north and lakeside of the facility behind the boiler house.

4.4.2 Fuel Storage Area

Coal for the EPA LIMB project and the DOE LIMB Demonstration Project Extension will be stored in the existing coal storage area which is approved by the Ohio EPA. This area is shown in the plot plan, Figure 4-4. Normally the facility stores a 45-day supply of coal or approximately 35,000 tons. During the LIMB and Coolside demonstration, up to 55,000 tons of coal will be stored on-site. The demonstration coal, which will be a higher sulfur coal than normally used, will be segregated from the regular coal, but stored on the same pad. Coal is delivered by truck, piled and compacted by bulldozer. Coal normally is delivered during the day shift. Normally 45-50 coal trucks come to the site in the eight-hour period. A small increase in the rate of truck unloading may be required to build inventory.

FIGURE 4-3. PLOT PLAN WITH NEW CONSTRUCTION SHADED.



1. PLANT BUILDINGS
2. TRUCK SCALE BUILDING
3. RAIL CAR LOADING AREA
4. YARD OFFICE

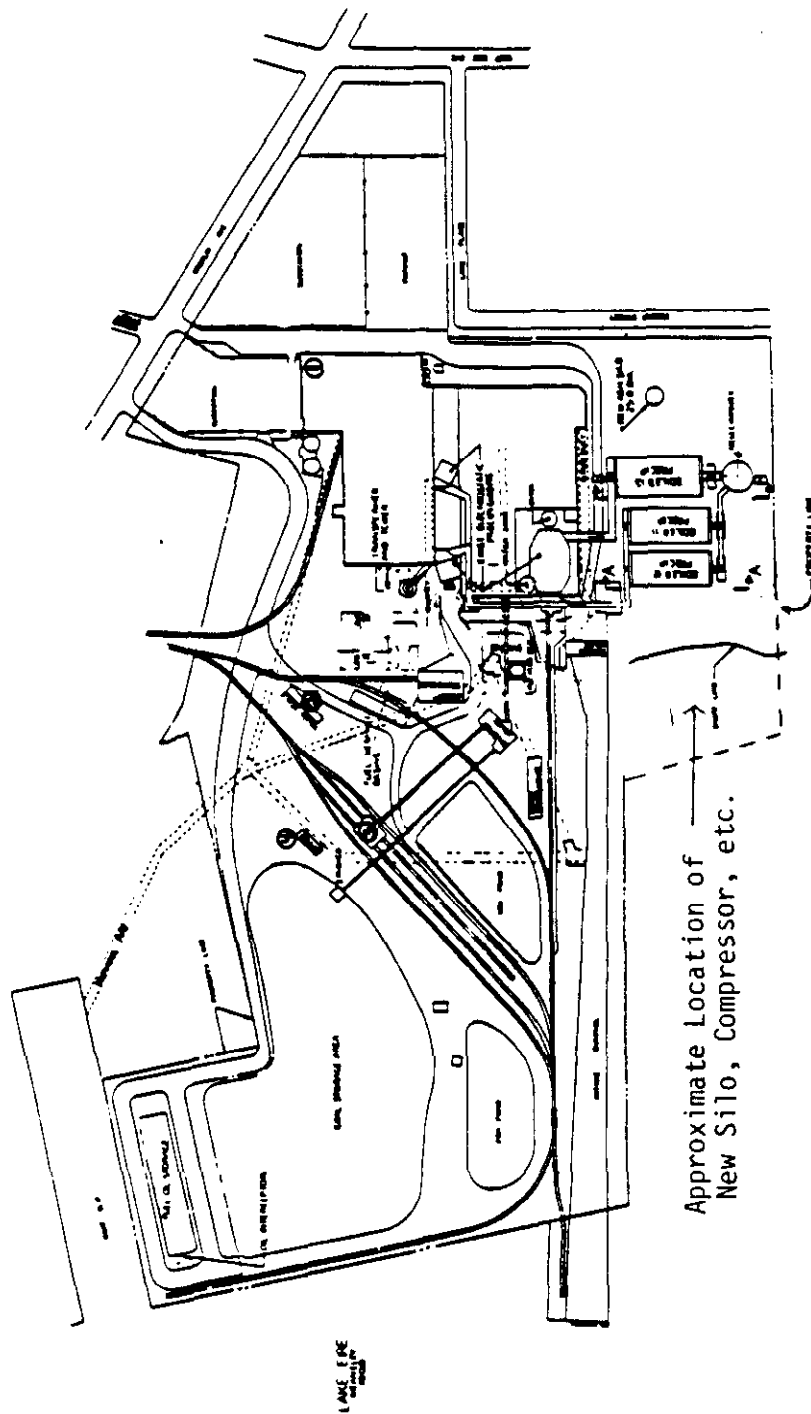


FIGURE 4-4.

REFERENCE DRWG.				DESCRIPTION				DATE				BY			
DRWG NO															
REV															
DATE															
BY															
OHIO EDISON CO.				DEPT. Production				PROJECT NO. 10378				SHEET NO. 10378			
ARSON, OHIO				PROJECT NO. 10378				PROJECT NO. 10378				PROJECT NO. 10378			
PROJECT NO. 10378				PROJECT NO. 10378				PROJECT NO. 10378				PROJECT NO. 10378			
PROJECT NO. 10378				PROJECT NO. 10378				PROJECT NO. 10378				PROJECT NO. 10378			

The existing coal storage pile is located on the northeastern side of the site and extends from the lake to the coal conveyor system. The main coal pile is approximately rectangular in shape with a width of 200 feet and length of approximately 350 feet. The pile is located on a pad of natural soil. The whole coal pile area is approximately 6 feet above the lake level and will be located in the flood plain according to our interpretation of the flood insurance rate map of the city of Lorain, Ohio, produced by the U. S. Department of Housing and Urban Development. Portions of the flood insurance map for the county are shown in Figure 4-5. Our interpretation of the figure and the limits of the flood zone A2 are shown in Figure 4-6. According to these figures, the northern 500 feet of the facility (everything north of the construction warehouse) is zone A2. Thus, the coal storage pile, the ash ponds and the limestone silo and new compressor are on the 100-year flood plain. The remainder of the site, south and west, is flood zone C, an area of minimal flooding.

4.4.3 Sorbent Storage Area

Sorbent for the LIMB Demonstration Project Extension will be delivered by bulk tanker truck and pneumatically conveyed to a new sorbent storage silo located immediately north of the existing silo behind the ESP No. 4.

4.5 OFF-SITE FACILITY REQUIREMENTS

The only additional off-site facility required for the project is a solid waste disposal area which is discussed further in Section 4.6.

No additional roadways are needed at the site for truck access, since all coal and ash is currently hauled by truck. Water will be supplied from Lake Erie or the plant's existing system. Any additional piping will be located on-site. No off-site transmission lines will be needed to supply power to the project.

4.6 IN-PLANT AND OVER-THE-FENCE DISCHARGES

The LIMB Demonstration Project Extension will produce gaseous, liquid and solid effluents during the operation. These are described in the applicable

CORPORATE LIMITS COINCIDE
WITH SHORELINE
(NORMAL WATER
ELEVATION)

WEST 1ST STREET ZONE B

WEST 2ND STREET

NO 5TH LAKE AVENUE

ERIE CITY HALL PLACE

WEST ASHLAND AVENUE WEST 5TH STREET

HAMILTON AVENUE

BROADWAY 577

ZONE C

ZONE A2 8/15/78

WEST 8TH STREET

WEST 9TH STREET

NORFOLK AND WESTERN RAILWAY

CHESIE STREET

ZONE B

ZONE C

AVENUE

AVENUE

WEST 15TH STREET

SYSTEM

611

FIGURE 4-5. PORTIONS OF FLOOD ZONE MAP FOR LORAIN AREA.

WES-


4-15

21ST

STREET

611

KEY TO MAP

500-Year Flood Boundary	—————→	
100-Year Flood Boundary	—————→	
Zone Designations* With Date of Identification - 12 2'74		
100-Year Flood Boundary	—————→	
500-Year Flood Boundary	—————→	
Base Flood Elevation Line With Elevation In Feet**		~~~~~ 513 ~~~~~
Base Flood Elevation in Feet Where Uniform Within Zone**		(EL 987)
Elevation Reference Mark		RM7 _x
River Mile		• M1.5

**Referenced to the National Geodetic Vertical Datum of 1929

*EXPLANATION OF ZONE DESIGNATIONS

ZONE	EXPLANATION
A	Areas of 100-year flood; base flood elevations and flood hazard factors not determined.
A0	Areas of 100-year shallow flooding where depths are between one (1) and three (3) feet; average depths of inundation are shown, but no flood hazard factors are determined.
AH	Areas of 100-year shallow flooding where depths are between one (1) and three (3) feet; base flood elevations are shown, but no flood hazard factors are determined.
A1-A30	Areas of 100-year flood; base flood elevations and flood hazard factors determined.
A99	Areas of 100-year flood to be protected by flood protection system under construction; base flood elevations and flood hazard factors not determined.
B	Areas between limits of the 100-year flood and 500-year flood; or certain areas subject to 100-year flooding with average depths less than one (1) foot or where the contributing drainage area is less than one square mile; or areas protected by levees from the base flood. (Medium shading)
C	Areas of minimal flooding. (No shading)
D	Areas of undetermined, but possible, flood hazards.
V	Areas of 100-year coastal flood with velocity (wave action); base flood elevations and flood hazard factors not determined.
V1-V30	Areas of 100-year coastal flood with velocity (wave action); base flood elevations and flood hazard factors determined.

NOTES TO USER

Certain areas not in the special flood hazard areas (zones A and V) may be protected by flood control structures.

This map is for flood insurance purposes only; it does not necessarily show all areas subject to flooding in the community or all planimetric features outside special flood hazard areas.

For adjoining map panels, see separately printed Index To Map Panels.

**FIGURE 4-6. KEY
FOR FIGURE 4-5.**

subsections below. Most of the discharges will occur during operation and very little impacts will occur during construction and disposition.

4.6.1 Air Emissions

Construction and operation of the LIMB Demonstration Project Extension will result in air emissions. These include fugitive dusts and vehicular emissions during construction, and vehicular emissions, power plant emissions and fugitive emissions during operations. The major air emissions will occur from the unit during demonstration. These are discussed in detail below.

Table 4-3 itemizes the expected Edgewater plant emissions and waste streams for the extended LIMB demonstration, with various coals of different sulfur content and each of four sorbents. The sorbents considered are hydrated calcitic lime, hydrated dolomitic lime, calcitic limestone and dolomitic limestone. Table 4-4 presents the same data for the Coolside process with one coal and one sorbent. Streams presented show SO_x , NO_x and particulate emission levels.

4.6.1.1 SO_2 Emissions. Currently the host site is discharging SO_2 at the rate of 2.44 lbs of SO_2 per million Btu. The LIMB technology proposes to reduce SO_2 emissions by up to 50 percent. In the parametric study where three coals of different sulfur contents and various sorbents are utilized, failure to maintain levels below the maximum SO_2 emissions standard of 3.4 lbs per million Btu will result in either of three control options:

1. The ratio of sorbent-to-sulfur in the coal will be increased in an attempt to capture more sulfur emissions. In general, the process will then be fine-tuned to ensure maximum SO_2 capture. If this proves unsuccessful in reducing SO_2 emissions to the desired levels, then;
2. Terminate the test on the particular coal-sorbent combination. The objectives of the test will have been met by virtue of finding that a particular coal-sorbent combination does not perform satisfactorily; or
3. Obtain a "hold harmless" clause to the air permit.

The Coolside technology is to be demonstrated on 3 percent sulfur content coal. A one MW demonstration of the Coolside process in 1984 showed that

TABLE 4-3. EXPECTED PLANT EMISSIONS AND WASTE STREAM

TOTAL NITROGEN OXIDE EMISSIONS (50% REDUCTION ASSUMED):

-Lbs/Hr at Full Load	509
-Tons/Yr (1)	960
-Lbs/Mbtu	0.48

SORBENT: HYDRATED CALCITIC LIME (BASE LINE DEMONSTRATION)

Coal Sulfur Level:	1.5%	3.0%	3.8%
--------------------	------	------	------

Total Sulfur Dioxide Emissions (50% Reduction Assumed):

-Lbs/Hr at Full Load	1237	2474	3134
-Tons/Yr (1)	2330	4660	5902
-Lbs/Mbtu	1.17	2.33	2.95

Total Particulate Emissions:

-Lbs/Hr at Full Load	65	97	114
-Tons/Yr (1)	122	183	215
-Lbs/Mbtu	0.06	0.09	0.11

Total Solid Waste (2):

-Lbs/Hr at Full Load	14587	22602	26870
-Tons/Yr (1)	27473	42568	50622
-Lbs/Mbtu	13.7	21.3	25.3

NOTES: (1) Assumed availability/capacity factor of 0.43

(2) Ash content of coal=10%; Ca/S stoichiometric ratio=2:1;
Neutralization by hydration

TABLE 4-3. EXPECTED PLANT EMISSIONS AND WASTE STREAM
(Continued)

SORBENT: HDRATED DOLOMITIC LIME

Coal Sulfur Level:	1.5%	3.0%	3.8%
Total Sulfur Dioxide Emissions(50% Reduction Assumed):			
-Lbs/Hr at Full Load	1237	2474	3134
-Tons/Yr (1)	2330	4660	5902
-Lbs/Mbtu	1.17	2.33	2.95
Total Particulate Emissions:			
-Lbs/Hr at Full Load	81	129	155
-Tons/Yr (1)	153	243	292
-Lbs/Mbtu	0.08	0.12	0.15
Total Solid Waste(2):			
-Lbs/Hr at Full Load	18066	29651	35692
-Tons/Yr (2)	34025	55675	67222
-Lbs/Mbtu	17.0	27.9	33.6

NOTES: (1) Assumed availability/capacity factor of 0.43
(2) Ash content of coal=10%; Ca/S stoichiometric ratio=2:1;
Neutralization by hydration

TABLE 4-3. EXPECTED PLANT EMISSIONS AND WASTE STREAM
(Continued)

SORBENT: CALCITIC LIMESTONE

Coal Sulfur Level:	1.5%	3.0%	3.8%
Total Sulfur Dioxide Emissions(50% Reduction Assumed):			
-Lbs/Hr at Full Load	1237	2474	3134
-Tons/Yr (1)	2330	4660	5902
-Lbs/Mbtu	1.17	2.33	2.95
Total Particulate Emissions:			
-Lbs/Hr at Full Load	71	109	129
-Tons/Yr (1)	134	205	243
-Lbs/Mbtu	0.07	0.10	0.12
Total Solid Waste(2):			
-Lbs/Hr at Full Load	16089	25607	30683
-Tons/Yr (2)	30302	48228	57788
-Lbs/Mbtu	15.2	24.1	28.9

NOTES: (1) Assumed availability/capacity factor of 0.43

(2) Ash content of coal=10%; Ca/S stoichiometric ratio=2:1;
Neutralization by hydration

TABLE 4-3. EXPECTED PLANT EMISSIONS AND WASTE STREAM
(Concluded)

SORBENT: DOLOMITIC LIMESTONE

Coal Sulfur Level:	1.5%	3.0%	3.8%
Total Sulfur Dioxide Emissions (50% Reduction Assumed):			
-Lbs/Hr at Full Load	1237	2474	3134
-Tons/Yr (1)	2330	4660	5902
-Lbs/Mbtu	1.17	2.33	2.95
Total Particulate Emissions:			
-Lbs/Hr at Full Load	89	145	175
-Tons/Yr (1)	168	273	329
-Lbs/Mbtu	0.08	0.14	0.16
Total Solid Waste (2):			
-Lbs/Hr at Full Load	25174	33350	40492
-Tons/Yr (2)	47413	62811	76263
-Lbs/Mbtu	23.7	31.4	38.2

NOTES: (1) Assumed availability/capacity factor of 0.43
(2) Ash content of coal=10%; Ca/S stoichiometric ratio=2:1;
Neutralization by hydration

TABLE 4-4. EXPECTED PLANT EMISSIONS, COOLSIDE DEMONSTRATION

Sorbent Hydrated Calcitic Limestone
Coal Sulfur Level 3%

Total sulfur dioxide emissions (75% SO₂ reduction assumed)

	<u>Once Through</u>	<u>Recycle</u>
- lbs/hr at full load	1,237	1,237
- tons/yr (1)	2,330	2,330
- lbs/MBtu	1.17	1.17
Total particulate emissions		
- lbs/hr at full load	63	62
- tons/yr (1)	119	117
- lbs/MBtu	.06	.057
Total solid waste (2)		
- lbs/hr at full load	21,047	18,556
- tons/yr	39,639	34,948
- lbs/MBtu	37.2	32.8

Notes: (1) Assumed availability/capacity factor of 0.43
(2) Once through design Ca/S = 2.0
3% sulfur coal NaOH/CaOH₂ = 0.1(w/w)
recycle design Ca/S = 1.6

75 percent SO₂ reduction can be expected at Edgewater. Based on these data, a maximum SO₂ emissions rate of 3.2 lbs of SO₂ per million Btu at a test condition which causes a 30 percent SO₂ reduction is projected for the host site during the Coolside optimization phase. During the Coolside demonstration phase, a 1.2 lbs of SO₂ per million Btu is projected. Taking into account that the test fuel will contain twice as much sulfur as the current fuel, this will lead to a net SO₂ reduction of 52 percent from current operating levels of Unit No. 4 during the Coolside demonstration.

4.6.1.2 NO_x Emissions. NO_x reduction will be realized by exchanging low-NO_x B&W XCL burners for the B&W circular burners currently in service at Edgewater. The predicted emission for the demonstration is 0.48 lbs of NO_x per million Btu based on recent tests conducted in EPA's large water tube simulator. Under normal conditions this would represent about a 50 percent reduction from what would be expected from a circular burner in a furnace built in the 1950's. Baseline testing of Edgewater unit No. 4 was conducted in May 1986 to characterize the unit prior to any LIMB modifications. Nine baseline NO_x tests were made and are summarized in Table 4-5. Average NO_x emissions ranged from 0.66 lb/MMBtu at a boiler load of 64 MW to 0.85 lb/MMBtu at a load of 101 MW. Based on these tests NO_x emissions reductions will range from 27 to 44 percent depending on boiler load.

4.6.1.3 Particulate Emissions. The predicted particulate emissions during the LIMB demonstration range from 0.06 lb/MMBtu to 0.16 lbs/MMBtu depending on the coal type and sorbent combination used. These predictions are based on an assumed particulate removal efficiency for the ESP of approximately 99.6 percent. Based on the permit requirements, particulate emissions must be maintained at or below 0.1 lbs per million Btu. The initial testing will include utilizing the ESP with a minimum number of fields energized. Information on the minimum fields required to keep particulate emissions below the limit is necessary to approximate a less conservative precipitator design characteristic of an average unit. Should the particulate level exceed the limit, more fields in the precipitator can be energized until the particulate emission limit is met.

The existing Lodge-Cottrell ESP was installed at Ohio Edison's Unit No. 4 in 1982 as a retrofit dust collector. It was designed to treat 412,627 acfm

TABLE 4-5. SUMMARY OF BASELINE CONTINUOUS MONITORING RESULTS
FOR NO_x AND SO₂ CORRECTED TO 3% OXYGEN

Boiler Load (MW)	Baseline Test No.	Corrected Stack Concentration (ppmv)		Stack Emission (lb/10 ⁶ Btu)	
		NO _x	SO ₂	NO _x	SO ₂
101	BL-01	586	2331	0.80	4.41
	BL-04	690	2552	0.94	4.83
	BL-06	<u>600</u>	<u>2616</u>	<u>0.82</u>	<u>4.95</u>
	Average	625	2500	0.85	4.73
82	BL-03	567	2679	0.77	5.07
	BL-08	600	2734	0.82	5.17
	BL-09	<u>600</u>	<u>2616</u>	<u>0.82</u>	<u>4.95</u>
	Average	589	2676	0.80	5.06
64	BL-02	464	2574	0.63	4.87
	BL-05	531	2602	0.72	4.92
	BL-07	<u>472</u>	<u>2490</u>	<u>0.64</u>	<u>4.71</u>
	Average	489	2555	0.66	4.83

of gas at 290⁰F and -13" wg at the ESP inlet. If the particulate loading at the inlet to the ESP is no greater than 21,602 lb/hr and the particulate resistivity is less than 10¹³ ohm-cm, the particulate emissions should be less than 0.1 lb/MMBtu according to Lodge-Cottrell.

The ESP has 316,800 square feet of collecting surface area resulting in a specific collection area (SCA) of 767. With this SCA and the projected resistivity of 10¹² ohm per centimeter, this ESP should have little trouble in achieving the required efficiency while the boiler is operating in the LIMB mode. If for any reason it is determined that the ESP will not perform adequately in this operational mode, flue gas conditioning such as humidification could be utilized to reduce the fly ash resistivity and bring the equipment into compliance with the emission requirements.

During the baseline testing, prior to installation of LIMB, particulate emissions and ESP efficiency measurements were made. Results of the EPA Method 5 testing at the ESP inlet and outlet are summarized in Table 4-6. As shown in Table 4-6, ESP inlet particulate loadings were similar for all three boiler loads, ranging from 3.55 to 3.71 grains/dscf. Average ESP outlet particulate loadings were also similar at 64 MW and 82 MW and approximately twice as high at 101 MW.

Particulate mass emission rates (lb/hr) at both the boiler outlet (ESP inlet) and the ESP outlet increased with increasing boiler load. Particulate mass rates at the boiler outlet ranged from 4,930 to 7,690 lb/hr and mass rates at the ESP outlet ranged from 35.4 to 108 lb/hr at boiler loads of 64 and 101 MW, respectively.

ESP removal efficiency was slightly lower for the high load tests (98.6 percent) compared with the two lower load tests (99.4 and 99.3 percent). The lower ESP efficiency and higher ESP inlet particulate loading at the high load test condition result in a correspondingly higher ESP outlet particulate emission on a heat input basis. Outlet particulate emissions averaged 0.093 lb/10⁶ Btu at the high load compared with 0.045 and 0.046 lb/10⁶ Btu at the two lower loads.

These results show that the ESP may not be operating as efficiently at high loads as assumed for the particulate emissions calculations and is

TABLE 4-6. SUMMARY OF BASELINE PARTICULATE LOADINGS AND MASS EMISSION RATES FOR THE ESP

Boiler Load (MW)	Baseline Test No.	M5 Run	Particulate Loadings (grains/dscf)		Mass Emissions (lb/hr)		Removal Efficiency (%)	Outlet Particulate Emissions (lb/10 ⁶ Btu)
			Inlet	Outlet	Inlet	Outlet		
101	BL-01	01	2.99	0.029	6260	62.3	99.0	0.054
	BL-04	04	3.77	0.061	8150	136.7	98.3	0.115
		05	3.70	0.041	8010	93.8	98.8	0.077
	BL-06	08	<u>4.38</u>	<u>0.068</u>	<u>8320</u>	<u>139.0</u>	<u>98.3</u>	<u>0.126</u>
	Average		3.71	0.050	7680	108.0	98.6	0.093
82	BL-03	03	3.99	0.017	6860	30.6	99.6	0.032
	BL-08	10	3.39	0.029	5600	49.6	99.1	0.057
	BL-09	11	3.49	0.029	5800	46.3	99.2	0.057
		12	<u>3.86</u>	<u>0.018</u>	<u>6620</u>	<u>31.5</u>	<u>99.5</u>	<u>0.035</u>
	Average		3.68	0.023	6220	39.5	99.4	0.045
64	BL-02	02	3.69	0.017	4890	23.5	99.5	0.032
	BL-05	06	3.55	0.023	5160	36.0	99.3	0.044
		07	3.69	0.020	5220	30.1	99.4	0.038
	BL-07	09	<u>3.28</u>	<u>0.037</u>	<u>4430</u>	<u>52.0</u>	<u>98.8</u>	<u>0.070</u>
	Average		3.55	0.024	4930	35.4	99.3	0.046

guaranteed by the vendor. However, this may be due to measurement of condensables in addition to particulate. Some method of measurements may be made to verify this.

4.6.1.4 Fugitive Emissions. The LIMB Demonstration Project Extension could potentially increase fugitive particulate emissions from the facility. Potential fugitive dust sources include sorbent unloading, the ash loading, the coal pile and the plant roads. The haul roads at the disposal site could also be a potential fugitive dust source. All of these sources will be controlled as required by the existing fugitive emissions permits.

The sorbent unloading operation will be pneumatic and will include a fabric filter on the silo to control emissions during unloading. All ash/spent sorbent generated during the demonstration will be stored in the existing ash silo prior to disposal. The dry material will be routed through a pug mill where the water will be added before the material drops into the dump truck for trucking to the disposal site. Wetting of the material will reduce the potential for fugitive dust emissions. After wetting, or mixing with water, the LIMB ash will get warm due to the hydration reactions and noticeable amounts of steam will be generated a short time after placing the material in the truck. It will be necessary to allow the truck to cool for a period before leaving the site. A tarped, 15 cubic yard dump truck with a disposable plastic liner or 20 to 25 cubic yard pushout truck with hydraulic ram will be used to remove the material and haul it to an Ohio EPA approved and licensed disposal site.

Several techniques are used to reduce the potential fugitive dust emissions from plant haul roads and parking areas. Fugitive dust emissions from paved surfaces are controlled by sweeping and water flushing on an as-needed basis. Unpaved surfaces are chemically treated with a dust suppressant once every three weeks or on an as-needed basis. In addition, haul trucks leaving the site are required to pass through a truck wash to reduce entrainment of material. All trucks leaving the site are covered. Fugitive dusts from the coal pile are controlled by compacting the material with a bulldozer. According to plant personnel, water sprays are not needed. All coal carrying conveyors and transfer points are enclosed and Ohio Edison

Company has a program to routinely inspect and repair all conveyor transfer points when necessary.

4.6.1.5 Vehicular Emissions. Construction material, coal, sorbent and ash will be transported to or from the site by truck. Air quality impacts from these mobile emission sources can be estimated. The emission factors for heavy-duty diesel-powered equipment are presented in Table 4-7. The major additional vehicular traffic to and from the site will be associated with delivery of sorbents and additional coal and disposal of ash. Sorbent delivery will result in a maximum of 12 additional trucks a day and ash/spent sorbent disposal will result in an additional 10 to 12 trucks. Additional coal delivery will result in a small increase in truck traffic. Using the emission factors shown in Table 4-7 the resulting carbon monoxide, hydrocarbon and NO_x emissions for the LIMB extension have been calculated, assuming that each truck makes a 30 mile round trip averaging five miles per gallon. Maximum expected vehicular emissions for the life of the project are 1.2 tons CO, 0.2 tons HC, and 2 tons NO_x . These are minimal compared with the current emissions from the power plant and mobile sources in the area.

4.6.1.6 Noise. The additional truck traffic and equipment needed for the LIMB Demonstration Project Extension will also contribute to the noise level in the area. However, the additional equipment is located behind the existing power plant and some 1,000 feet from the noise sensitive area. In addition, the noise will occur against a background of the ambient operational noise from other power plant activities and would not represent a significant impact.

4.6.1.7 Air Permits. It is not anticipated that any additional air permits will be necessary for demonstration over and above those already obtained for the base LIMB demonstration. Presently the Edgewater facility holds an operating permit issued by the state of Ohio on August 3, 1984, with an expiration date of August 3, 1987. In addition to this permit, a variance was applied for as part of the base LIMB technology demonstration to allow burning of high sulfur coal to develop baseline data on boiler performance with high sulfur coal prior to lime injection into the boiler. The variance was approved. After the high sulfur coal case, one goal of the LIMB

TABLE 4-7. EMISSION FACTORS FOR HEAVY-DUTY, DIESEL-POWERED EQUIPMENT

EMISSION FACTORS FOR GIVEN EQUIPMENT					
POLLUTANT	Heavy-duty Truck (lb/ 1000 Gallons)	Wheeled Tractor (lb/hour)	Wheeled Dozer (lb/hour)	Off-High- way Truck (lb/hour)	Miscel- laneous (lb/hour)
Carbon Monoxide	225	2.15	0.74	1.34	0.41
Hydro- carbons	37	0.15	0.23	0.44	0.16
Nitrogen Oxides	370	0.99	5.05	7.63	2.27

Source: U.S. Environmental Protection Agency, 1976a. Compilation of Air Pollutant Emission Factors, Second Edition (revised through 1976) AP-42, Research Triangle Park, North Carolina.

Demonstration Project Extension is to assure that the present emission limits at Edgewater of 0.1 lbs particulate per million Btu and 3.4 lbs SO_x per million Btu on a rolling 30-day average are not exceeded.

4.6.2 Wastewater Emissions

There are five wastewater streams generated or affected by the LIMB Demonstration Project Extension. These are the ash water discharge, drainage from lime handling, acid storage tank drainage, drainage from the lime silo enclosure, and coal pile stormwater runoff. These are described briefly below.

4.6.2.1 Ash Water Discharge. The discharge from the ash handling system hydraulic exhauster is an existing wastewater discharge which is directed to the ash pond. This stream presently contains some coal fly ash carryover from the ash silo bag filter. On LIMB, the stream flow remains the same at approximately 1,000 gpm; however, this stream will change in that the ash carryover could now contain as much as 44 percent calcium oxide (lime), thereby making the stream alkaline. The ash water pH control system is designed to neutralize this alkalinity by injecting sulfuric acid into the discharge line. Thus, despite the increase in waste stream pH, the final ash pond discharge will be maintained at the present pH of about 7 to 8. The discharge will, however, be high in suspended solids. The ash water pH control system will be conservatively designed to ensure that pH levels in the final discharge will be within permitted limits.

4.6.2.2 Lime Handling and Storage Area Discharge. Spills of pulverized lime may be experienced in the lime handling and storage area. Proper housekeeping practices will provide for manual cleanup and removal of major quantities of spilled lime with possible periodic maintenance washdowns to the lime area drain. Additionally, precipitation runoff from this area will be routed to this wastewater drain. Drainage will be conveyed to the bottom ash dewatering bin sump for subsequent recycle or treatment in the ash pond. Drainage quantity and quality will vary depending on the activity generating it; however, at worst it will be high in suspended solids and alkalinity.

4.6.2.3 Acid Storage Tank Area Drainage. The new 5,000 gallon sulfuric acid storage tank of the ash water pH control system is located in a concrete

diked area sized to retain the full tank volume in the event of tank rupture plus precipitation from a 10 year, 24 hour rainfall event. A collection sump with crushed limestone is located within this area. The gravity discharge line from the sump has a normally closed valve which can be used to direct drainage to a plant wastewater collection trench. Periodically, the pH of the precipitation collected in the sump will be monitored and if acceptable (pH of 6 to 9) the sump valve will be opened to drain the sump. This discharge will likely contain some suspended solids. The sump will drain to the ash pond, but this drainage will not affect the final ash pond discharge. Large acid spills would require manual neutralization and cleanup. The crushed limestone will serve to neutralize small amounts of sulfuric acid which may drip from the tank fill connection during filling operations.

4.6.2.4 Drainage From Lime Silo Enclosure. Noncontact cooling water will be discharged from the sorbent feed pump compressor (about 10 gpm) and storage silo fluidizing air refrigerant air dryer (about 12 gpm) to a floor drain and ultimately to the bottom ash dewatering bin sump. The drainage will be of lake water quality with an elevated temperature (120°F, approximately). The temperature rise to lake water will be insignificant. At this time there is some question about where the noncontact cooling water will be discharged. An option is to discharge the water into the main plant cooling water intake.

4.6.2.5 Coal Pile Stormwater Discharge. During the demonstration period, high sulfur coals will be stockpiled on the existing coal pile. This is expected to affect the coal pile stormwater discharge by slightly lowering the pH and increasing the dissolved metals and solids content of the runoff. However, the magnitude of these effects is dependent on the level of coal impurities, and cannot be predicted until a test coal is selected. The effects on Lake Erie are expected to be insignificant compared to the effects of the ash pond discharge.

4.6.2.6 Wastewater Permits. The basic water pollution control obligations imposed on the Edgewater power plant originate from the federal Clean Water Act and provisions of the Ohio water pollution control laws. With the LIMB and Coolside technologies, no significant changes in quantity or quality of water discharged over Edgewater's present status is anticipated

except the pH and total suspended solids. To deal with this possibility, a pH control system will be installed to assure maintenance of pH at existing permit levels.

The major additional wastewater stream from the Coolside demonstration project will be the noncontact cooling water used by the compressor supplying atomizing air to the humidification nozzles. This compressor unit utilizes approximately 250 gpm of water. Some of this water (approximately 74 gpm) will be used to humidify the flue gas, and the remainder will be discharged into the intake channel. Other waste streams will remain largely unchanged.

The facility is currently filing for a modification to the existing NPDES permit for the additional discharges which are small compared with the existing power plant streams. All wastewater from the LIMB Demonstration Project Extension will eventually drain through the primary ash pond and then through the secondary ash pond prior to discharge. The current permit specifies sampling and analysis for pH, total suspended solids, oil & grease, and various metals. Limits have been set for pH, total suspended solids, and oil & grease. There is a potential that wastewater from the LIMB process will increase the pH and the suspended solids levels.

4.6.3 Solid Wastes

The largest volume waste stream from the project will be the combined spent sorbents and ash from the LIMB Demonstration Project Extension. The estimated quantity of solid waste produced for each of the four sorbents is summarized in Tables 4-3 and 4-4.

The solid wastes produced will be fly ash from coal combustion combined with excess lime and calcium sulfate. Coolside waste product will include calcium sulfite as well as calcium sulfate and some increase in sodium because of the additive used. The total solid waste production rate for the Edgewater Unit No. 4 will be in the region of 21 acre-feet a year (46,200 tons/year). This includes water of hydration and assumes a 43.3 percent unit capacity factor.

4.6.3.1 LIMB Ash Leachate Studies. Ash by-products from the LIMB process were investigated in a pilot-scale facility by Southern Research Institute (SoRI). An average of 11 analyses of the ash generated by SoRI is

presented in Table 4-8. The ash consists primarily of excess lime, calcium sulfate and the coal's fly ash.

There is concern over whether the high pH of the leachate from this material will cause disposal problems. Utility wastes such as fly ash and scrubber sludge are in an exempt category under the Resource Conservation and Recovery Act. Under this act, an extraction procedure (EP toxicity test) is used to leach out metals normally considered pollutants of concern. In tests conducted by SoRI thus far, metals extracted from LIMB ash were below the concentration used to define hazardous waste (see Table 4-9). The quicklime component of the ash is beneficial in this regard since its chemically basic nature suppresses solubilization of many of these metals.

The addition of water to LIMB ash is expected to result in cementitious reactions producing a material with increased structural integrity and lower permeability in a manner similar to the technique of mixing wet scrubber sludge with fly ash and lime. Stabilizing the material in this fashion may reduce or eliminate the potential need for neutralization of leachate.

Under an EPA/SoRI cooperative project on disposal, recycle and by-product use of LIMB ash, SoRI is currently evaluating options of producing a synthetic aggregate for use as a road base material. In this case, a controlled hydration step would be required. SoRI is also working on several tasks including permeability studies of stabilized ash and characterization of runoff samples from West Lorain.

4.6.3.2 Permeability Studies on West Lorain Core Samples. Ash conditioning tests were performed at Edgewater with LIMB ash from the Lakeview Station of Ontario Hydro. The wetted ash was transported to a test section on the property surrounding the West Lorain Plant of Ohio Edison. Ten piles of conditioned ash were placed in the landfill section. Samples were removed from each truck at the plant site. These samples were analyzed for free lime, sulfur, metal oxides, carbon, and hydrogen. A thermogravimetric analysis in a nitrogen atmosphere was performed on the Lakeview ash to determine calcium carbonate content.

From this analysis, it was determined that the free lime content of the ash was approximately 24 percent, instead of the 17 percent which was

TABLE 4-8. LIMB ASH ANALYSES GENERATED BY SOUTHERN RESEARCH INSTITUTE
(SoRI) IN A PILOT-SCALE FACILITY

Component	Range of Values % by Weight
Loss on ignition	2.0 - 4.2
Li ₂ O	0.01
Na ₂ O	0.11 - 0.15
K ₂ O	0.38 - 0.78
MgO	0.70 - 0.77
CaO	36.7 - 51.1
Fe ₂ O ₃	3.8 - 12.1
Al ₂ O ₃	5.5 - 10.4
SiO ₂	9.3 - 21.7
TiO ₂	0.4 - 0.7
P ₂ O ₅	<0.03 - 0.05
SO ₃	15.5 - 26.8

TABLE 4-9. LEACHATE ANALYSIS OF ASH (EP TOXICITY TEST)

Specie	<u>Concentrations in Leachate, mg/l</u>		Levels Which Define Hazardous Waste mg/l
	Sample A	Sample B	
Arsenic	0.0145	0.0210	5
Barium	4.11	4.24	100
Cadmium	0.00095	<0.0005	1
Chromium	0.0394	0.0240	5
Lead	<0.0030	0.0045	5
Mercury	<0.0003	0.0003	0.2
Selenium			
Silver	<0.0005	<0.0005	5
pH	12.4/12.2 pH units ^a	12.4/12.2 pH units ^a	12.5 max.

^aBefore/after acid addition

estimated by B&W before the wetting tests were run on the ash (Tables 4-8 and 4-9). This information changed the water:lime ratios slightly so that the ratios were in the range of 2.5-4.0 instead of the 3.5-5.5 previously thought.

To determine permeability of water through the ash piles, core samples were to be taken at 4 weeks, 16 weeks and 32 weeks, or until the permeability coefficient was <0.000001 cm/s. On August 19, 1986, some core samples were removed from the landfill site by SoRI. Law Engineering ran their permeability test on the specimen in the sampling cylinder without removing it first. The permeability coefficient was 8×10^{-4} cm/s, which is very high for this type of product after this length of curing (approximately 4 weeks). Dravo Lime Company had gotten a permeability of 3.6×10^{-6} cm/s for samples made in their laboratory and cured for 30 days. Therefore, a better method had to be devised to remove the core samples. A suggestion was made to use concrete coring and drilling equipment and cores were subsequently taken.

Table 4-10 gives the results of tests performed to date. The ash piles with the actual water:lime ratios of 3-3.6 gave fairly good results, but the best results came from the pile which set up like cement (Pile #5). During the wetting test for this pile, the pugmill tripped off line several times so that large quantities of water occasionally poured into the pugmill while no ash was flowing into it. At other time, the conditioning system worked properly to give the lower water:lime ratios desired, but the truckload included a high water content for some parts, while other parts had considerably lower contents. The overall consistency was described as mudlike. No estimate of an overall water:lime ratio could be made.

4.6.3.3 Characterization of Runoff Samples From West Lorain Landfill Test Cell. On July 23-25, ash was received from Ontario Hydro, conditioned with various water:lime ratios at Edgewater using a Dravo-Wellman conditioning system, and placed in separate piles in a lined 40 by 60 foot area. Ohio Edison collected samples of the runoff from the drainage trench and sump and submitted them to SoRI for determination of solids, pH alkalinity, and RCRA metals.

Table 4-11 lists the samples and the results obtained to date. In some cases a composite sample was used to provide enough sample for analysis.

TABLE 4-10. CORE SAMPLES FOR PERMEABILITY TESTING
FROM EDGEWATER LANDFILL

<u>SRI Sample #</u>	<u>B & W Sample #</u>	<u>B&W Water:Lime Ratio</u>	<u>SRI Water:Lime Ratio</u>	<u>Permeability Ratio Coefficient, cm/sec</u>
D-0754-14- 1	3A'-A	4.5:1	3.2:1	6.75×10^{-4}
D-0753-14- 2	3A'-B	4.5:1	3.2:1	---
D-0753-14- 3	3A	4.5:1	3.2:1	1.46×10^{-4}
D-0753-14- 4	3B	4.5:1	3.2:1	---
D-0753-14- 5	3C	4.5:1	3.2:1	4.78×10^{-4}
D-0753-14- 6	5A'	Sludge	--	1.71×10^{-6}
D-0753-14- 7	5A	Sludge	--	---
D-0753-14- 8	6A'-A	5:1	3.6:1	3.64×10^{-4} ^a
D-0753-14- 9	6A	5:1	3.6:1	1.0×10^{-6} ^b
D-0753-14-10	6B	5:1	3.6:1	9.49×10^{-6}
D-0753-14-11	7A'-A	Operators Discretion	2.9:1 - 3.6:1	2.9×10^{-5}
D-0753-14-12	7A'-B	Operators Discretion	2.9:1 - 3.6:1	3.29×10^{-5}
D-0753-14-13	7A	Operators Discretion	2.9:1 - 3.6:1	---
D-0753-14-14	7B	Operators Discretion	2.9:1 - 3.6:1	4.01×10^{-5}
D-0753-14-15	A'	Operators Discretion	2.9:1 - 3.6:1	3.63×10^{-6}
D-0753-14-16	A	Operators Discretion	2.9:1 - 3.6:1	3.11×10^{-4} ^a

^a These two samples were not sealed properly, so the permeability is higher than expected.

^b Tested by Law Engineering using back pressure permeability method.

TABLE 4-11. ANALYSIS OF RUNOFF SAMPLES FROM WEST LORAIN LANDFILL TEST CELL

Sample Description				Sample Analysis													
Sample No.	Date	Time	Location	Approx vol, mL	TSS, mg/L	Alkalinity as CaCO ₃ , mg/L			Concentration, mg/L								
						pH	P	a	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium	Silver	
D0753-10-4	7/20/86	11:10 am	SW	100	230	12.0	--	--									
D0753-11-6	7/20/86	11:06 am	NW	150													
			Composite														
D0753-13-1	7/20/86	11:17 am	Sump	300	5.5	6.8	--	--	0.007	1.4	<0.000	<0.005	<0.003	<0.001	<0.005	<0.0001	
D0753-10-1	7/29/86	8:30 am	S	100	251	11.6	150	210	<0.002	7.1	<0.0005	0.014	<0.003	<0.001	<0.005	<0.0001	
D0753-11-11	7/29/86	8:30 am	W	100													
D0753-11-4	7/29/86	8:30 am	W	150													
			Composite														
D0753-12-1	7/29/86	8:30 am	Sump	300	17	7.1	--	--	<0.002	6.1	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001	
D0753-10-2	7/30/86	9:45 am	S	100	300	11.4	54	80	0.004	7.4	<0.0005	0.027	<0.003	<0.001	<0.005	<0.0001	
D0753-9-7	7/30/86	9:45 am	DS	150													
D0753-11-5	7/30/86	9:45 am	W	200													
			Composite														
D0753-13-2	7/30/86	9:45 am	Sump	300	22	7.2	--	74	0.004	1.8	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001	
D0753-10-3	7/31/86	9:15 am	S	100	885	11.5	162	193									
D0753-13-4	7/31/86	9:15 am	R	150													
D0753-13-7	7/31/86	9:15 am	NAC	100													
			Composite														
D0753-12-2	7/31/86	9:15 am	Sump	300	6.9	7.2	--	89	0.005	2.2	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001	
D0753-11-8	8/2/86	10:30 am	NW	100	82	7.8	--	--									
D0753-9-4	8/2/86	10:05 am	Sump	150	8.4	7.2	--	--									
D0753-11-2	8/3/86	8:30 am	SW	100	1620	6.9	--	--									
D0753-11-9	8/3/86	8:30 am	NW	150													
			Composite														
D0753-13-3	8/6/86	8:30 am	Sump	300	26	7.5	--	--	<0.002	2.6	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001	
D0753-8-6	8/19/86	--	S		156	7.6	--	66	0.009	14	0.0014	0.072	0.008	<0.001	<0.005	0.0007	
D0753-8-7	8/19/86	--	Sump		8.5	7.7	--	92	0.003	2.1	0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001	
D0753-8-8	8/19/86	--	Sump														

a. Not determined, sample inadvertently acidified after pH measurement.

TABLE 4-11. ANALYSIS OF RUNOFF SAMPLES FROM WEST LORAIN LANDFILL TEST CELL (Continued)

Sample Analysis																		
Sample No.	Date	Time	Location	Approx vol, mL	TSS, mg/L	Alkalinity as CaCO ₃ , mg/L			Concentration, mg/L									
						pH	P	S	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium	Silver		
00153-16-1	8/7/86	1:30 pm	SWP			7.5												
-19-5			SEC			7.4												
-19-6			S			7.1												
-19-7			S			7.3												
-19-8			S			7.3												
-17-1	8/7/86	5:30 pm	SWP			7.1												
-19-1			EM			6.8												
-19-9			S			7.8												
-20-4			W			7.0												
-20-8			W			7.0												
-17-2	8/8/86	12:30 pm	SWP			7.7												
-19-2			E			7.1												
-20-9			W			7.3												
-17-3	8/10/86	4:20 am	SWP			7.0												
-17-4			SWP			6.9												
-19-3			SEC			7.1												
-20-5			W			6.9												
-20-10			W			7.0												
-17-5	8/11/86	4:30 am	SWP			7.2												
-17-6	8/12/86	10:30 am	SWP			7.2												
-17-7	8/13/86	1:00 pm	SWP			7.1												
-17-8	8/16/86	10:00 am	SWP			7.3												
-17-9	8/15/86	3:00 pm	SWP			7.2												
-19-10			S			7.0												
-20-11			W			7.3												
-17-10	8/18/86	2:00 pm	SWP			7.5												
-17-11		3:00 pm	SWP			7.3												
-17-12	8/20/86	11:30 am	SWP			7.3												
-18-1	8/21/86	6:00 am	SWP			7.3												
-18-2		11:30 am	SWP			7.3												
-18-3	8/22/86	7:00 am	SWP			7.3												
-18-4		11:00 am	SWP			7.4												
00153-18-5	8/23/86	7:00 am	SWP			7.3												
-18-6		7:30 pm	SWP			7.2												
-18-7	8/24/86	11:00 am	SWP			7.4												
-18-8	8/25/86	2:30 pm	SWP			7.5												
-18-9		3:00 pm	SWP			7.4												
-18-10	8/26/86	9:30 am	SWP			7.0												
-19-11			S			7.8												
-20-6			W			6.8												
-20-12			W			7.1												
-19-4	8/27/86	9:30 am	EM			7.2												
-18-11	8/29/86	1:30 pm	SWP			7.3												
-20-1			SE			7.7												
-20-2			S			7.7												
-20-3			S			7.3												
-20-7			W			7.3												

Figure 4-7 gives a layout of the West Lorain test area so the location of the sample can be referenced.

The total dissolved solids were determined using Method 160.2 Residue, Non-Filterable, and the pH was determined using Method 150.1 Electrometric.¹ Mercury, selenium and barium were determined by Methods 245.1 Cold Vapor, Manual; 270.3 Atomic Absorption, Gaseous Hydride; and 208.1 Atomic Absorption, Direct Aspiration, respectively.¹ The rest of the RCRA metals were determined using the Atomic Absorption, Graphite Furnace methods found in Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020. Alkalinity was determined using Method 403 found in Standard Methods for the Examination of Water and Wastewater.²

4.6.3.4 Disposal Site. The ultimate disposal site for the LIMB and Coolside ash has not yet been selected. One area being considered is the Ohio Edison solid waste landfill where flyash is presently being disposed. In addition, the Ohio Edison Company has issued an inquiry for removal and disposal of ash from the site. In the inquiry Ohio Edison have the following specifications for the disposal site.

1. The disposal site shall be licensed by the Ohio EPA for solid waste disposal and be operating in good standing.
2. The ash shall be disposed of in accordance with all applicable environmental regulations.
3. The ash will be segregated in the disposal site to allow for long term observation and testing of the ash by U. S. EPA and others.
4. The contractor shall dispose of the ash in a safe and lawful manner and shall not in any manner salvage, reclaim, reuse, sell or distribute the ash without prior written approval of the company.

¹Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020.

²Standard Methods for the Examination of Water and Wastewater, 15th Edition, Mary Ann H. Franson, Editor, American Public Health Association, Washington, D.C., 1980, p. 253-257.

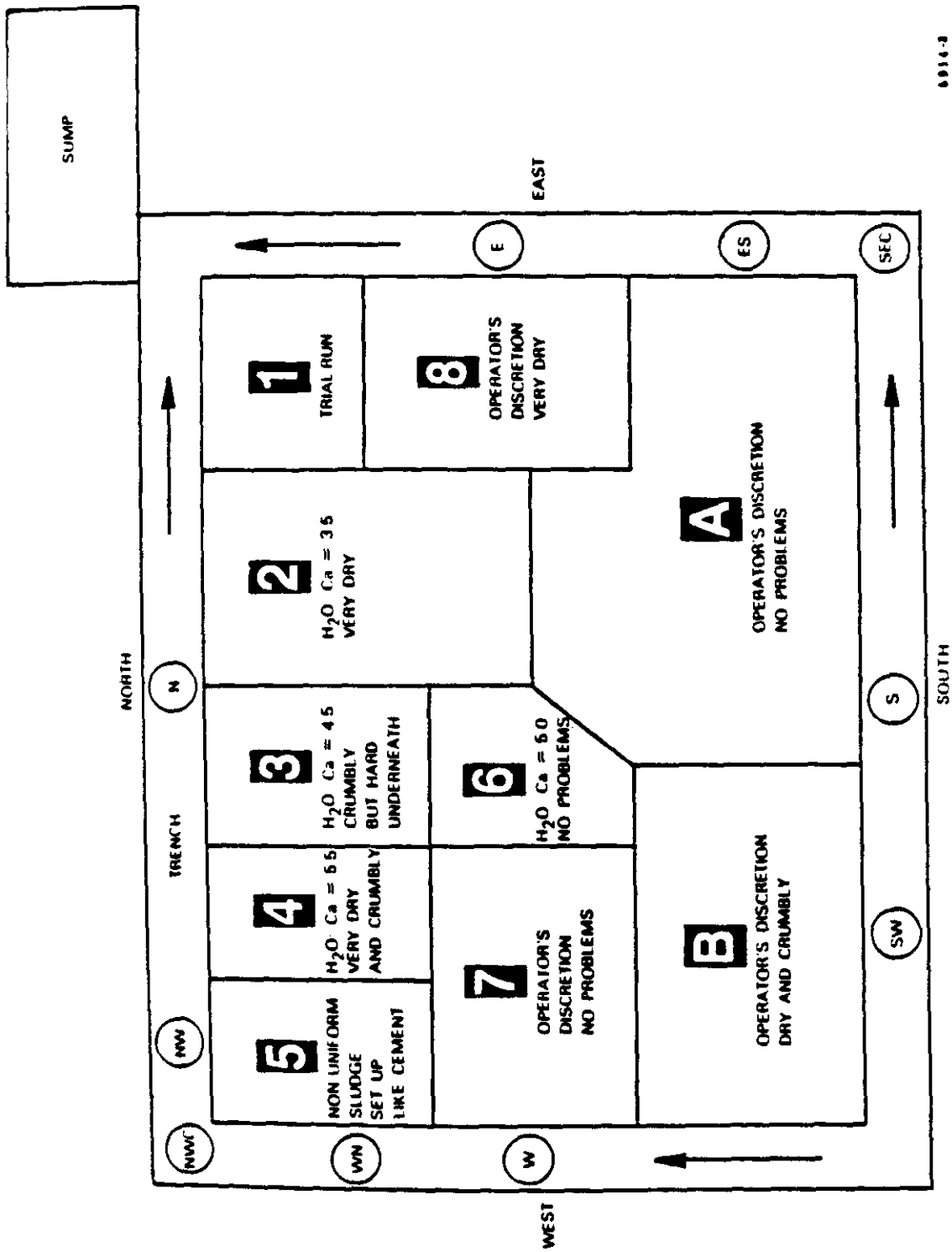


FIGURE 4-7. LOCATIONS OF RUNOFF SAMPLES TAKEN AT THE WEST LORAIN LANDFILL TEST SITE

Since the disposal site has not been selected the exact applicable regulations and requirements are not available; however, some idea of the level of discharge requirements can be obtained by considering the limits specified for the runoff from the West Lorain area. These are as follows:

pH 6-9 and total suspended solids: Monthly average, 30 ppm; maximum daily, 100 ppm.

As can be seen from Table 4-11, the pH in the trenches was initially 12 on 7/28. However, after five days, the pH dropped to about 7. The pH in the sump remained around 7 for all the samples tested, probably due to dilution from rain water. Since the allowable pH discharge limits for landfill runoff are 6 to 9, there seems to be no problem with the pH in the sump or in the trenches after five days. In all of the samples reported, the RCRA metals were well below the maximum allowable limit. The total suspended solids ranged from 82 to 1,620 ppm in the trenches and 5 to 26 ppm in the sump. Again there does not seem to be a total suspended solids problem in the sump. However, the trenches were all above the monthly average discharge, and most samples were above the maximum limit. In the trenches the p alkalinity ranged from 54 to 162 ppm and the m alkalinity ranged from 66 to 210 ppm. The m alkalinity ranged from 74 to 92 ppm in the sump. Currently there are no alkalinity regulations for a landfill.

The results indicate that runoff from the ultimate disposal site should be contained and directed to a monitored sump or holding pond before discharge. There appears to be no correlation between the total suspended solids and time, or alkalinity and time.

4.6.3.5 Coolside Ash Characteristics. There is less information on Coolside ash characteristics than is available for LIMB ash. Available data from pilot plant work and for ash from similar processes are summarized here.

Table 4-12 presents the projected Coolside waste composition. The Coolside ash differs from LIMB ash in several ways. For example, there is less residual free lime in the Coolside ash, and a larger fraction of calcium sulfite. The spent sorbent will require less water because water is required

TABLE 4-12. PROJECTED COOLSIDE WASTE COMPOSITION AND QUANTITY*

<u>Component</u>	<u>Once Through Option, pph</u>	<u>Recycle Case pph</u>
Ca(OH) ₂	7,288	4,969
CaSO ₄	820	874
CaSO ₃	4,099	4,373
Na ₂ SO ₃	1,375	1,091
Na ₂ SO ₄	274	217
Flyash	<u>7,191</u>	<u>7,032</u>
Total	21,047	18,556

* Once Through Design Basis Ca/S = 2.0, 75% SO₂ removal, 3% sulfur coal
NaOH/Ca(OH)₂ = 0.1 (w/w)

Recycle Design Basis Ca/S = 1.6, 75% SO₂ removal, 3% sulfur coal
NaOH/Ca(OH)₂ = 0.1 (w/w)

only for fugitive dust control during pug milling and disposal. Temperature rise is not a problem since fully hydrated sorbent is injected into the flue gas duct downstream of the airheater. The waste also contains appreciable concentrations of sodium salts which may increase the total dissolved solids content of the leachate. Available EP toxicity test results are summarized in Table 4-13.

There are no compressive strength or permeability data for Coolside residue per se; however, information on these properties is available for spray dryer residues for the Joy/NIRO SO_2/NO_x process which, similar to Coolside, involves injection of sodium hydroxide as an additive in conjunction with lime. These data are summarized in Table 4-14. The pure SO_2 product is normal spray dryer residue, and the SO_x/NO_x product is the spent sorbent and sodium hydroxide additive. Landfilling of the Coolside residue should present no unusual problems based on the above cited data.

TABLE 4-13. EP TOXICITY TEST RESULTS, mg/L

Metal	Allowable Limit (RCRA)	Martinsville (Conoco)			Simulated LMB Waste (B&W)	
		Coal Ash	Coal Ash	BLT Fly Ash	Coal Ash/Mercer Hydrate	Coal Ash/Marblehead Hydrate
Calcium		491	2006	3407		
Sodium		70.6	1008	10.2		
Potassium		12.2	13.6	4.35		
Magnesium		38.2	21	33		
Silicon		19.9	0.52	0.41		
Arsenic	5	0.014	0.002	0.002	0.021	0.0145
Barium	100	0.090	1.801	1.174	4.24	4.10
Cadmium	1	0.012	<0.001	<0.001	<0.0005	<0.00095
Chromium	5	<0.005	0.038	0.059	0.024	0.0394
Lead	5	<0.001	<0.004	<0.010	<0.0044	<0.003
Mercury	0.2	<0.002	<0.002	<0.002	<0.0003	<0.0003
Selenium	1	<0.005	0.023	0.020	0.0228	0.0296
Silver	5	<0.025	<0.025	<0.025	<0.0005	<0.0005
Total Dissolved Solids	500*	2245	9516	11605		
pH	12.5 max	5.1	12.2	12.4	12.2	12.2

*Guideline only, not regulation.

TABLE 4-14. COMPRESSIVE STRENGTH AND PERMEABILITY OF
PURE SO_x AND COMBINED SO_x/NO_x PRODUCTS*

COMPRESSIVE STRENGTH (kPa)	PURE SO ₂ PRODUCT	SO _x /NO _x PRODUCT
1 DAY	120	110
7 DAYS	180	200
30 DAYS	480	340
56 DAYS	600	580
PERMEABILITY (10 ⁻⁶ cm/s)		
1-2 DAYS	2.5	6
28 - 30 DAYS	-	-

* All samples are compacted to 960-980 kg/m³ in dry density

5.0 CONSEQUENCES OF THE PROJECT

5.1 CONSEQUENCES OF CONSTRUCTION

The consequences of construction of the LIMB Demonstration Project Extension will be minimal, since little additional construction will be required for the LIMB extension project over and above what is already planned for the EPA LIMB work.

It should be noted that it is difficult to separate the impacts of the DOE LIMB Demonstration Project Extension from the impacts of the original EPA LIMB proposal or modifications. Much of the hardware/construction needed by the DOE LIMB Demonstration Project Extension projects will have already been built when the portion of the project which is the focus of this environmental report begins. Currently, plans are to install the necessary limestone delivery and ash handling equipment, bypass duct, and humidification equipment prior to the initiation of the DOE LIMB Demonstration Project Extension. The bypass duct is to be financed under the DOE LIMB project. Additional construction includes ash/sorbent recycle piping, additive mixing and injection, all of which are minor components.

5.1.1 Environmental, Health, and Safety Impacts

The site of the proposed demonstration plant is an existing industrial complex. Therefore, on-site construction activities are expected to have minimal impact. This is especially true since virtually all of the construction for the LIMB process extension will have already taken place for the EPA LIMB demonstration. Only installation of an ash recycle system and rerouting of the sorbent distribution piping and installation of additive injection is necessary for the Coolside demonstration since the construction for the humidification portion of the project will have been completed under the EPA LIMB.

5.1.1.1 Atmospheric Impacts, Including Projection of Air Quality Degradation. The impacts of the construction of the DOE LIMB facility on the ambient air quality should be minimal due to the type of activities involved, such as forming and pouring concrete and placing process equipment, and those

impacts will be limited as much as is practicable to the site location. Since very small areas of the site are to be disturbed, fugitive particulate emissions from construction will be minimal. The construction equipment and trucks will generate small amounts of CO, THC, and NO_x, but these are not significant compared to the amounts of these compounds presently generated by the facility and vehicles in the vicinity.

5.1.1.2 Hydrologic Impacts, Including Changes in Ground Water/Surface Water Quality and Quantity, and Stream Diversion. The hydrological impacts of this project during construction will be negligible. The construction area is very small, and excavation will be minimized to the extent possible. Diversion berms will be constructed around the excavated areas to prevent any run-on. Stormwater within the excavated areas is expected to seep into the ground. There will be no stream diversions during the construction period. There will be no withdrawal of ground water for construction purposes.

5.1.1.3 Land Use Impacts During and After Construction Activities. Land use impacts at the facility will be minimal primarily due to the fact that alteration of existing environs has previously taken place through industrial development of Ohio Edison Company's Edgewater Plant, the location for the planned construction. Impacts that will occur should be temporary in nature, revolving around construction-related activities. Any impacts caused by the use of irretrievable resources will be recognized and the appropriate corrective action will be taken if necessary.

5.1.1.4 Public and Occupational Health Consequences of Construction Activities, Including Accidents. It is not envisioned that any facet of the LIMB Demonstration Project Extension construction and demonstration will impose any unusual or unique health or safety hazards to employees or the public. The small quantities of additives used in the Coolside process will be handled in a manner consistent with the MSDS recommendations to ensure workers' and environmental safety.

The proposed construction will be undertaken with the health and safety of all employees uppermost in mind. As part of its function as construction manager, B&W prepares safety specifications to be followed by all contractors. The responsibilities of all contractors with regard to the Occupational Safety and Health Act (OSHA) and state safety codes are specified in the B&W safety

specifications. Often, depending on the nature of the construction activities, special requirements will be imposed on the contractor. This is handled on a case-by-case basis before the award of the contract.

During operation of the demonstration, power plant safety personnel will be on site. Routine safety meetings and any required monitoring activities will be coordinated by these personnel in compliance with all regulations in accordance with current Ohio Edison practice.

5.1.1.5 Ecological Impacts. Babcock and Wilcox foresees no measurable ecological impacts due to construction. Because the site of the proposed facility is an existing industrial complex, construction activities will be short term and performed under appropriate permits, and since no sensitive aquatic or terrestrial habitats are located nearby, there should be no impact on the ecological community.

5.1.2 Socioeconomic Impacts

Construction of the Demonstration Facility is projected to require approximately 50 workers at peak activity. The construction period for this plant is forecast to be approximately six months. Effects of the added construction workers are expected to be experienced largely in the immediate area. This area is the host county of Lorain where most primary impacts are to be realized. Impacts will be dispersed throughout the adjoining region based on proximity to urban areas, work force origins, and transportation networks. It is expected that a considerable number of the new construction workers will be current residents of the Lorain areas.

5.2 CONSEQUENCES OF OPERATION AND DISPOSITION OF THE PROJECT

The consequences of operation of the project are more significant than the consequences of construction. This section will discuss the atmospheric impacts, hydrologic impacts, land use impacts and other significant impacts of operation.

5.2.1 Atmospheric Impacts

The goal of the LIMB Demonstration Project Extension is to reduce both NO_x and SO_x emissions from the station, and if the demonstration is successful, there will be a positive impact on air quality for these

pollutants. The particulate emissions from the facility may increase if the Coolside and LIMB humidification technologies are not able to enhance ESP performance to the degree expected since additional particulate matter is being introduced into the gas stream ahead of the electrostatic precipitator. However, the gas stream is being controlled by an oversized ESP. The LIMB Demonstration Project Extension may also affect fugitive particulate emissions from the facility. Any effect on fugitive dust should be minimal since all dry sorbent handling equipment is furnished with baghouse filters. The waste material is more tightly bonded with reference to dusting than is the present flyash material.

In general, the operation of the LIMB Demonstration Project Extension will result in a decrease in SO_2 and NO_x , but may have a potentially negative impact on particulate levels. Each of these impacts is discussed briefly below.

Currently the host site is discharging SO_2 at a rate of 2.44 lbs of SO_2 per million Btu. It is expected that the LIMB technology will reduce SO_2 emissions by up to 50 percent. In a parametric study where three coals of different sulfur content (1.5, 3.0 and 3.8 percent) and various sorbents are utilized as proposed, failure to maintain levels below the maximum SO_2 emissions standard of 3.4 lbs of SO_2 per million Btu permitted for the plant will result in either of two control options: 1) the ratio of sorbent to sulfur in the coal will be increased in an attempt to capture more sulfur emissions. In general the process will then be fine-tuned to ensure maximum SO_2 capture. If this proves unsuccessful in reducing SO_2 emissions to desired levels, then 2) terminate the test on that particular coal/sorbent combination. The objectives of the test will have been met by virtue of finding that a particular coal/sorbent combination does not perform satisfactorily. The demonstration will then move on to the next coal/sorbent combination.

The Coolside technology is to be demonstrated utilizing a 3.0 percent sulfur content coal. The major variables for the Coolside processing controlling the SO_2 emissions are the calcium:sulfur ratio, and the amount of additive used with the lime. If required, an increase in sorbent or additive

feed rates will be used such that the SO_2 emissions do not exceed the current limit at the host site. A one MW field test program of the Coolside process in 1984 showed 75 percent SO_2 reduction can be expected. Based on these data, maximum SO_2 emission rates of 3.2 lbs of SO_2 per million Btu at a 30 percent SO_2 reduction test condition is projected from the host site during the Coolside optimization phase. During the Coolside demonstration phase, a 1.2 lbs of SO_2 per million Btu emission rate is projected. Taking into account that the test fuel will contain twice as much sulfur as the current fuel, this will lead to a net SO_2 reduction of 52 percent from current operation levels of Unit No. 4 during the Coolside demonstration.

NO_x reduction will be realized by exchanging low NO_x B&W XCL burners for the B&W circular burners currently in service at Edgewater. The predicted emission for the demonstration is 0.48 lbs of NO_x per million Btu based on recent tests conducted in EPA's large water tube simulator facility operated by EER in El Toro, California. If these levels are achieved, NO_x emissions reduction will vary from 27 to 44 percent depending on boiler load.

Particulate emissions must be maintained at or below .1 lbs per million Btu. Results of the baseline testing showed that emissions without LIMB were close to this limit. It is anticipated that the particulate emissions will increase with the injection of sorbent into the boiler or flue gas since load on the electrostatic precipitator will be increased. It would be expected that with a very conservatively designed unit as at Edgewater, the excess capacity in the ESP would serve as a buffer to ensure particulate emissions do not exceed the limitation during the period of operating when the system is optimized. Flue gas humidification during the LIMB extension program and as an integral part of the Coolside technology will also improve precipitator performance. This, in addition to the excess capacity of the ESP, makes the probability of exceeding particulate limitations less during the demonstrations. Predicted particulate emissions without humidification range from 0.06 to .16 lb/MBtu. At an emissions rate of 0.16 lb/MBtu the predicted maximum ground level impact will be 22 ug/m^3 . This result is based on scaling the results of five year modeling (using ISCST Model, Urban Mode 3) for determination of SO_2 impact from the station. Only 8 ug/m^3 of this impact is

attributable to emissions above permitted levels (.16 lb/Mm Btu to .1 lb/Mm Btu).

Based on the Ohio ambient monitoring data for TSP in Lorain County for 1981 presented in Table 5-1, the additional 8 ug/m^3 will not cause exceedences of the 24-hour primary standard of 260 ug/m^3 at any monitoring station that is currently in compliance. However, it should be noted that one monitoring station exceeded the primary standards in 1981 and two stations exceeded the secondary 24-hour standard of 150 ug/m^3 . As a result, the station exceedences may exacerbate some air quality issues in the area. Given the short-lived nature of the project and the ability to increase particulate removal efficiency by humidification, the adverse impacts attributable to exceeding the permit limits will be small.

Fugitive particulate emissions from on-site operations such as coal unloading and storage, plant haul roads and ash and sorbent handling should be controlled adequately if the existing fugitive emission permit requirements are followed. Fugitive emissions from landfilling the residues will also be small if the residue is slaked prior to disposal.

5.2.2 Hydrologic Impacts

The hydrologic impacts from the LIMB Demonstration Project Extension will be small. Some changes to the ground water underlaying the coal storage pile can be expected from the storage of high sulfur coal which will generate a more acidic leachate. The original coal used at Edgewater contained approximately three percent sulfur and was considered a high sulfur coal. Therefore, comparable leachates have been generated in the past.

No increase in the volume of runoff from the coal power is expected since the area covered by the storage pile cannot be increase due to the site space limitations. However, some decrease in pH and increase in dissolved metals, solids and total acidity content of the runoff can be expected as a direct result of lower pH. Metals and acidity levels in the runoff are primarily dependent on their level in the coal, not on the coal-sulfur content, and cannot be predicted until a test coal is selected. The lowering of pH in the coal power runoff is due primarily to the air oxidation of the iron sulfides in the coal as shown in the following equation:

SITE SUMMARY OF TOTAL PARTICULATES
UNITS: MICROGRAMS/CUBIC METER (25 DEG.C)
JAN 31-DEC 31

STATE/ASCA/COUNTY:		AREA	SITE	SIP	FED	ANNUAL	TOTAL	TOTAL	TOTAL	2ND	3RD	4TH	5TH	SFD
				REQ	AGE	GEQ	24-MR	24-MR	24-MR	24-MR	24-MR	24-MR	24-MR	SEC
				SITE	YEAR	AVG	ORR	ORR	ORR	ORR	ORR	ORR	ORR	ORR
4369 OHIO														
(174) METROPOLITAN CLEVELAND INTRASTATE AGRIC														
(3288) LAKE COUNTY														
WICKLIFFE														
	367300001602	29240 EUCLID AVENUE		Y	01	53.9	57	0	0	141-	105-	89-	83-	1-53
WILLCUSHBY														
	367400003602	30345 APOLLO PKWY		Y	01	56.3	59	0	0	130-	115-	104-	103-	1-55
WILLOUGHBY HILLS														
	367460001003	2882 CRICKET LAKE		Y	01	42.8	55	0	0	101-	92-	79-	76-	1-56
WILLOWICK														
	367480001601	301 EAST 293RD STREET		Y	01	47.9	55	0	0	144-	105-	79-	78-	1-58
(3649) LORAIN COUNTY														
AVON LAKE														
	368340005631	150 AVON NELDON RD		Y	01	45.8	53	0	0	184-	102-	94-	86-	1-63
ELVIRA														
	361900001F01	925 SPRUCE ST		Y	01	45.7	56	0	0	133-	95-	83-	82-	1-57
LORAIN														
	363620003F02	6 STREET LORAIN		Y	01	65.2+	56	0	4	241.+	191.+	162.+	141-	1-79
	3065F01	2276 E 42ND ST		Y	01	51.5	54	0	0	130-	87-	82-	77-	1-41
	014F02	2615 COLORADO LORAIN		Y	01	103.4+	10 Y	1	4	379.+	259.+	165.+	129-	1-82
	026F01	NEBRASKA AHO ADAMS		Y	01	36.6	9 Y	0	0	81-	52-	47-	42-	1-73
OSCEOLA														
	365140001F01	132 ARTINO ST		Y	01	43.2	53	0	0	91-	87-	69-	69-	1-48
(4163) MEDINA COUNTY														
MEDINA														
	364140001401	MEDINA PUBLIC SQUARE		Y	01	53.9	55	0	0	91-	90-	84-	84-	1-39

NOTE: THIS REPORT MAY CONTAIN SITES FOR WHICH TOTAL OBSERVATIONS (TPO) DO NOT MEET SAMPLING CRITERIA SUFFICIENT FOR ANNUAL SUMMARY

*** = EXCEEDS PRIMARY STANDARD *** = EXCEEDS SECONDARY STANDARD

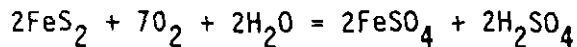


Table 5-2 presents some coal storage runoff data by coal sulfur content. This data was derived by EPA and may be used at the first cut for estimating the pH of the runoff from the high-sulfur coal. By interpolation, the runoff from the high-sulfur coal will lower the pH to approximately 2.6. It should be realized that the existing coal power runoff will have a pH of around 3 and that the change in runoff pH of just .4 of a pH unit may not be very significant in terms of impacts on the ash pond.

Surface water impacts from operation of the projects will be small compared with the existing impact from the coal-fired station. There are no significant wastewater discharges from LIMB and Coolside in comparison with the Edgewater power plant discharges. The character of the discharges may change due to sorbent infiltration into the sluice water. This could result in a higher effluent pH. A system for pH adjustment will be installed to ensure compliance with effluent limitations. The wastewater generated with LIMB and Coolside technology retrofit to a power plant is not expected to be unique as compared with a conventional coal fired power plant without these retrofit technologies.

The hydrologic impacts from solid waste disposal cannot really be quantified at this time. The SoRI work showed that the runoff from disposed material was neutral after a short period of time and also had low levels of metals. In addition, the permeability of the disposed material was low and if the disposal site is properly sited then the waste handled should be no additional problem. The initial runoff from the waste disposal site will have a high pH and high total suspended solids. It may be necessary to provide runoff collection and pH adjustment for the portion of the disposal site (i.e., less than seven days old) to mitigate these impacts. In addition, the ground water in the selected solid waste disposal area may increase in pH and may have higher total dissolved solids.

5.2.3 Land Use Impacts

Land use impacts at the LIMB Extension Facility will be minimal since the demonstration project is taking place at an existing site and very little

TABLE 5-2. COAL STORAGE PILE RUNOFF DATA

Coal Sulfur %	very low	2.0%	4.2%	high
Runoff pH	6.6	2.81	2.56	2.1
Runoff Concentration (mg/l)				
Acidity	9	3350	1650	21,700
Sulfate	--	5160	3050	19,000
TDS	--	7900	3600	28,970
Iron	1	940	350	4,700
Aluminum	--	260	43	1,200
Mn	--	28.7	4.1	--
Zn	--	6.46	2.42	12.5

Cox, Doye, B., et al. 1979. EPA-600/7-79-051.

additional land will be used. Disposal of solid waste from a demonstration project may have a noticeable impact. As previously discussed, up to 20 acre-feet of waste material will be generated in a year (including 5 acre-feet of ash that would be generated without LIMB), and it can be expected that 30-40 acre-feet of material will be generated over the life of the demonstration project. Assuming fill depths of up to 10 feet, 3 to 4 acres of land would have to be committed instead of approximately 1 acre for the existing station for long term disposal of the waste product. One positive benefit of waste disposal in a separate facility is that the existing life of the presently used landfill will be extended for one to two years. This issue will be more fully addressed when the final disposal site is selected.

5.2.4 Geologic Impacts

The demonstration project will cause negligible geologic impacts to soils at the Edgewater site. However, there may be some geologic impacts from the solid waste disposal. This cannot be addressed at this time.

5.2.5 Public and Occupational Health and Safety Impacts

It is not envisaged that any facet of the LIMB Demonstration Project Extension construction and demonstration will impose any unusual or unique health or safety hazards to employees or the public. The small quantities of additive used in the Coolside process will be handled in a manner consistent with the material safety data sheet recommendations to ensure workers' and environmental safety. The solid waste generated will exhibit some of the properties of calcium oxide and will require handling in an appropriate manner when it is being disposed. Again, the recommendations contained in the material safety data sheets for lime and similar materials will be followed when the material is handled.

The LIMB Extension will result in an increased volume of truck traffic to the plant. Some 20 to 24 additional trucks will enter the plant every day for delivering lime or trucking off of additional ash. This is compared with 45 to 50 trucks under existing situations. This may increase the noise levels on the access roads to the Edgewater station, and will result in a small increase in NO_x , CO, and THC in the area over the life of the project.

5.2.6 Ecological Impacts

The demonstration project will have no known or predicted ecological impacts at the Edgewater station since it is an existing power plant and there is no suitable habitat on-site. There is some potential for ecological impacts at the solid waste disposal site. However, these cannot be quantified since the site has not been selected at this time.

5.2.7 Impact on Regional or Local Plans for Fuel and Water Resources

The LIMB Demonstration Project Extension will have a beneficial impact on any plans for coal utilization in the area since the project will use locally mined medium and high sulfur coal. The impact on water resources is negligible compared with the existing station. Total estimated water use for the LIMB Extension is discussed further in Section 7.0.

The impacts of the solid wastes may be significant since solid waste volumes will increase two to four times depending on the sorbent type and ratio used.

5.2.8 Irreversible/Irretrievable Commitment of Resources

The LIMB Demonstration Project Extension will consume approximately 180,000 tons of coal including 60,000 tons of 1.5 percent sulfur, 60,000 tons of 3 percent, and 60,000 tons of 3.8 percent. This will replace the coal currently used by the station. The project will also consume 9,000 tons of calcitic limestone, 16,000 tons of dolomitic limestone, 8,000 tons of dolomitic hydrated lime and 2,500 tons of promoted lime. The Coolside technology demonstration will consume approximately 60,000 tons of 3 percent sulfur coal, and 6,000 tons of sorbent. An additional 1,200 tons of additive (50 percent sodium hydroxide) will be consumed.

The spent sorbent material may be recycled for uses such as neutralization of acid wastes and production of synthetic aggregate for roads. Research into potential beneficial reuse is being made by Southern Research Institute at this time.

5.2.9 Socioeconomic Impacts

Long term beneficial socioeconomic attributes of the LIMB and Coolside technologies are expansion of the nation's coal mining sections and fuel price stabilization. Jobs and incomes will be created as coal mining operations are

expanded to allow use of higher sulfur coals than can be used with current SO₂ emission restrictions. The higher sulfur coals are generally lower in price and therefore have a positive impact on utility economics. The availability of a broader number of coals as candidate fuels will induce electricity price stabilization as the utility will now have an increased latitude on fuel options while not exceeding SO₂ emissions. Jobs and income created as coal mining operations are expanded would be immediately filled in southwestern Ohio where coal is the largest contributor to the economy according to the Ohio Mining and Reclamation Assn. However, the impacts on jobs and the economy based on the LIMB demonstration project alone would be small and short-lived since the project will only last for two years or so. Impacts on the labor force will be minimal but slightly positive. It is anticipated that no additional operating labor will be required at the station; however, some additional labor will be on-site during the demonstration project to ensure proper operation of the equipment and to obtain the necessary performance data (2 to 3 people maximum).

5.2.10 Aesthetic Impacts

No aesthetic or visual impacts are anticipated from demonstration of the technology at the Edgewater site. Some impacts may result in the selected solid waste disposal area.

5.2.11 Impact on Tribal or Other Religious Practices

There should be no impact on tribal or religious practices from the LIMB Demonstration Project Extension technologies at the Edgewater plant.

6.0 REGULATORY COMPLIANCE

The environmental regulations with which the technology will have to comply are those regulations governing air quality and emissions, water quality and discharges, and solid and hazardous wastes with which the present power plant must comply prior to retrofit with the proposed SO_x/NO_x reduction technology. Health and safety regulations directed at employees will continue to be met in the same manner as in the case prior to retrofit.

6.1 AIR REGULATIONS

Air emissions from the Edgewater plant are governed by appropriate attainment and non-attainment area regulations of the Clean Air Act. Non-attainment regulations apply where the National Ambient Air Quality Standards (NAAQS) are not being met for specific criteria pollutants. Criteria pollutants for which there are NAAQS are listed below.

- Sulfur dioxide (SO_2)
- Carbon monoxide (CO)
- Total suspended solids (TSP)
- Nitrogen dioxide (NO_2)
- Photochemical oxidants
- Lead

The Edgewater plant is located in a designated attainment area for SO_x emissions and secondary non-attainment area for TSP.

As discussed in earlier sections, the LIMB and Coolside technologies will reduce both NO_x and SO_x emissions from the facility and compliance will be maintained. In addition, a variance of the operating permit was applied for as part of the base LIMB technology demonstration to allow burning of high sulfur coal during baseline testing.

The particulate emissions from the facility may exceed allowable limits during portions of the LIMB extension project if humidification is not utilized. However, this will be for a short duration, and the need for another variance to the air permit to cover these periods is not anticipated.

As part of the LIMB Demonstration Project Extension, Radian Corporation will be on-site throughout the period to monitor gas composition and collect solid and liquid samples for analysis. Data that will be obtained includes continuous emissions monitoring to measure CO, CO₂, O₂, SO_x, NO_x and hydrocarbons. Manual gas analyses and particulate sampling will also be conducted. This information, along with the data from B&W system 140 monitoring the furnace and routine operating data, will be sufficient to characterize the operation and performance of the boiler and LIMB system on each coal/sorbent combination. These results will provide the basis for evaluating SO₂ removal performance, ESP efficiency and process control ability. It is not anticipated that any additional environmental data collection will be needed beyond that already required by the applicable permits and/or regulations since much environmental data is being conducted as part of the demonstration process. All monitoring data obtained for permit compliance will be submitted to the appropriate agencies as required by the permits. These data are available to the general public from the agencies. Additional environmental data collected, if useful, will be made available through technical publications.

6.2 WASTEWATER REGULATIONS

The basic water pollution control obligations imposed on the Edgewater power plant originate from the federal Clean Water Act and the provisions of the Ohio water pollution control laws. The permit requirements for the station are summarized in Table 6-1. According to Ohio Edison personnel, the facility is in compliance with the applicable limits. Some modifications may be required to the current NPDES permit for discharge of the additional wastewater through the existing outfalls. This is currently being investigated. As previously discussed, the pH and TSS of the ash pond discharge may change. To deal with this possibility, a system for pH adjustment will be installed to ensure maintenance of pH at existing permit levels. No additional provisions will be made to control total suspended solids.

TABLE 6-1. NPDES PERMIT SUMMARY

<u>Edgewater</u>	
St. No. 31800005	
Fed. No. OH0031306	
<u>Influent</u>	801 & 802
TSS, mg/l	No Lmt/2 Per Week Grab (802)
Oil, mg/l	-----
Temp	No Lmt/Daily Cont. (801)
pH, S.U.	-----
Phos, mg/l	No Lmt/Monthly Grab (802)
<u>Cooling Water</u>	001
pH, S.U.	6-9 Monthly Grab
Flow, MGD	No Lmt/24 hour Ttl Est
Thermal Load	-----
T.R. Cl ₂ , mg/l *	0.2/Daily Grab
F.A. Cl ₂ , mg/l *	-----
Temp	No Lmt/Daily Cont.
Phos, mg/l	No Lmt/Monthly Grab
<u>Ash Ponds</u>	601
Flow, MGD	No Lmt/2 Per Week 24 hour Ttl Est
pH, S.U.	6-9/2 Per Week Grab
TSS, mg/l	30-100 Hot/2 Per Week Grab
Oil, mg/l	15-20/Monthly Grab
Arsenic, ug/l	No Lmt/Monthly Grab
Iron, ug/l	-----
Copper, ug/l	-----
Phos, mg/l	No Lmt/Monthly Grab
<u>Floor Drains</u>	N/A
Flow, MGD	
pH, S.U.	
TSS, mg/l	
Oil, mg/l	
<u>Sanitary</u>	To City Sewer
Color	
Odor	
Turbidity	
Flow, MGD	
BOD ₅ , mg/l	
TSS, mg/l	
pH, S.U.	
Fecal Coliform, /100ml	
T.R. Cl ₂ , mg/l *	
<u>Boiler Blowdown</u>	606
Flow, MGD	No Lmt/24 hour Ttl Est
pH, S.U.	No Lmt/Weekly Grab
TSS, mg/l	30-100 Weekly Grab
Iron, ug/l	-----
Copper, ug/l	-----
Oil, mg/l	-----
Phos, mg/l	15-20/Monthly Grab
<u>Oil Separator</u>	002
Flow, MGD	No Lmt/Monthly 24 hour Ttl Est
Oil, mg/l	15-20/Monthly Grab
pH, S.U.	6-9/Monthly Grab
Phos, mg/l	No Lmt/Monthly Grab
<u>Hydro and Oil Cooling</u>	N/A
Flow, MGD	
Temp. °F	
<u>Transformer Cooling</u>	N/A
Flow, MGF	
Temp. °F	
<u>Slag Tank Overflow</u>	N/A
pH, S.U.	
TSS, mg/l	
Flow, MGD	

* T.R. = Total Residual, F.A. = Free Available.

6.3 SOLID WASTES

Disposal of solid wastes from the facility is governed by the State of Ohio Waste Disposal Regulations. The solid wastes will be disposed of in an Ohio EPA approved landfill if they cannot be sold. A disposal site for the LIMB and Coolside residues has not yet been selected, and therefore a permit for landfilling the solid wastes has not yet been obtained.

7.0 INFORMATION TO DETERMINE IMPACTS TO WATER RESOURCES

Water resource requirements and water availability are not significant issues for this project when compared with existing water use at the Edgewater station. The station water use is presented in Figure 7-1. The power plant uses some 110 Mgd for once-through cooling water and approximately 1 Mgd for process water. The LIMB extension and Coolside demonstration projects' estimated water usage is presented in Table 7-1. The projects will require a maximum water usage rate of 450 gpm. Water needed for humidification will be taken from the compressor cooling water discharge. This stream may also be used to slake the LIMB and Coolside residues. Actual water demand will then be reduced to 250 gpm. This is less than 1 percent of the total water demands of the site and is judged inconsequential. Any water needed and consumed by the project will be supplied by Lake Erie which is virtually an inexhaustible resource.

TABLE 7-1. WATER USAGE FOR LIMB DEMONSTRATION AND COOLSIDE

	LIMB	Coolside
Noncontact cooling water for compressors	22 gpm	250 gpm
Hydrovac water usage current 1,000 gpm	Unchanged from original	Unchanged from original
Humidification	0	74 gpm
Slaking of residues (10% excess) or pugmilling	50-100 gpm	4 gpm
Fugitive dust control	Unknown--no additional from base plant	Unknown--no additional from base plant
Additive dilution	0	2 gpm

APPENDIX B
PROCEDURES FOR WASTEWATER AND SOLID WASTE ANALYSIS

CALCIUM

Method 215.2 (Titrimetric, EDTA)

STORET NO. Calcium (mg/1 CaCO₃) 00910

Calcium, Total (mg/1 Ca) 00916

1. Scope and Application
 - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
 - 1.2 The lower detection limit of this method is approximately 0.5 mg/1 as CaCO₃; the upper limit can be extended to all concentrations by sample dilution. It is recommended that a sample aliquot containing not more than 25 mg CaCO₃ be used.
2. Summary of Method
 - 2.1 Calcium ion is sequestered upon the addition of disodium dihydrogen ethylenediamine tetraacetate (EDTA). The titration end point is detected by means of an indicator which combines with calcium only.
3. Interferences
 - 3.1 Strontium and barium interfere and alkalinity in excess of 30 mg/1 may cause an indistinct end point. Magnesium interference is reduced or eliminated by raising the pH between 12-13 to precipitate magnesium hydroxide.
4. Apparatus
 - 4.1 Routine laboratory titrimetric glassware
5. Reagents
 - 5.1 Sodium hydroxide, NaOH, 1 N
 - 5.2 Indicators
 - 5.2.1 Many indicators are available, both laboratory prepared and commercial, and may be used. Two are described here.
 - 5.2.2 Murexide (ammonium purpurate) indicator: This changes from pink to purple. Dissolve 150 mg of the dye in 100 g absolute ethylene glycol. If a dry powder is preferred mix 200 mg murexide with 100 g solid NaCl and grind to 40 to 50 mesh. Titrate immediately after adding indicator because it is unstable under alkaline conditions.
 - 5.2.3 Eriochrome Blue Black R (sodium-1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid) indicator: This changes from red through purple to bluish purple to a pure blue without any trace of red or purple tint. The pH of some waters must be raised to 14 (rather than 12-13) by the use of 8 N NaOH in order to get a good color change. Grind in a mortar 200 mg powdered dye and 100 g solid NaCl to 40 to 50 mesh. Store in tightly stoppered bottle. Use 0.2 g of this mixture for titration.

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5.3 Standard EDTA titrant, 0.02 N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 \cdot 2 \text{H}_2\text{O}$ in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (5.3.1) by titration (5.3.5). Store in polyethylene. Check periodically because of gradual deterioration.

5.3.1 Standard calcium solution, 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in heavy metals, alkalies and magnesium) in a 500 ml flask. Add, a little at a time 1 + 1 HCl (5.3.2) until all of the CaCO_3 has dissolved. Add 200 ml distilled water. Boil for a few minutes to expel CO_2 . Cool. Add a few drops of methyl red indicator (5.3.3) and adjust to intermediate orange color by adding 3N NH_4OH (5.3.4) or 1 + 1 HCl (5.3.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water.

5.3.2 Hydrochloric acid solution, 1 + 1

5.3.3 Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in a 100 ml volumetric flask and dilute to mark.

5.3.4 Ammonium hydroxide solution, 3 N

5.3.5 Standardization titration procedure: Place 10 ml standard calcium solution (5.3.1) in a vessel containing about 50 ml distilled water. Add 1 ml buffer solution (5.3.6). Add 1-2 drops indicator (5.3.7) or small scoop of dry indicator (5.3.7). Titrate slowly with continuous stirring until the last reddish tinge disappears, adding last few drops at 3-5 second intervals. At end point the color is blue. Total titration duration should be ≤ 5 minutes from the time of buffer addition.

$$\text{N of EDTA} = \frac{0.2}{\text{ml EDTA}}$$

5.3.6 Buffer solution: Dissolve 16.9 g ammonium chloride in 143 ml conc ammonium hydroxide in a 250 ml volumetric flask. Add 1.25 g of magnesium salt of EDTA (5.3.8) and dilute to the mark with distilled water. Store in tightly stoppered plastic bottle.

5.3.7 Indicator: Commercially available Eriochrome Black T is used in one of the three methods described. All gradually deteriorate.

5.3.7.1 Mix 0.5 g dye with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 ml of 95% ethanol or isopropanol.

5.3.7.2 Place 0.5-1.0 g dye in 100 g of triethanolamine or 2-methoxyethanol.

5.3.7.3 Mix 0.5 g dye and 100 g NaCl for dry formulation.

5.3.8 EDTA Magnesium Salt: Commercially available.

6. Procedure

6.1 Pretreatment

6.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 6.2.

6.1.2 For most wastewaters and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 6.2.

6.2 Sample Preparation:

6.2.1 The calcium content of the 50 ml aliquot to be titrated should be 5-10 mg, therefore dilution should be used for high calcium concentrations.

- 6.2.2 If the alkalinity is > 300 mg/1 CaCO_3 and cannot be reduced by dilution because of low calcium concentration, the alkalinity must be decreased by acidifying, boiling one minute and cooling.
- 6.3 Titration
- 6.3.1 Add 2.0 ml NaOH solution (5.1), or a volume sufficient to produce pH 12 to 13, to 50 ml of sample.
- 6.3.2 Stir. Add 0.1 to 0.2 g indicator (5.2.2 or 5.2.3) or 1–2 drops if indicator solution is used.
- 6.3.3 Immediately titrate with continuous stirring. Check to see that no further color change occurs when using murexide (5.2.2) by adding 1 to 2 more drops of titrant after recording milliliters of titrant at first judged end point.
7. Calculations
- 7.1 Total calcium
- $$\text{mg/1 Ca} = \frac{A \times N \times 20,040}{\text{ml of sample}}$$
- where:
- A = ml titrant
- N = Normality of EDTA solution
- 7.2 Calcium hardness
- $$\text{mg/1 CaCO}_3 = \frac{A \times N \times 50,000}{\text{ml of sample}}$$
- where A and N are the same as in 7.1.
8. Precision and Accuracy
- 8.1 A synthetic unknown sample containing 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/1 Na, 241 mg/1 chloride, 1.1 mg/1 nitrate N, 250 μg /1 nitrite N, 259 mg/1 sulfate, and 42.5 mg/1 total alkalinity in distilled water was determined by this method with a relative standard deviation of 9.2% and a relative error of 1.9% in 44 laboratories.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 189, Method 306C (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D511–76, Method B, p 253 (1976).

FLUORIDE

Method 340.2 (Potentiometric, Ion Selective Electrode)

STORET NO: Total 00951

Dissolved 00950

1. Scope and Application
 - 1.1 This method is applicable to the measurement of fluoride in drinking, surface and saline waters, domestic and industrial wastes.
 - 1.2 Concentration of fluoride from 0.1 up to 1000 mg/liter may be measured.
 - 1.3 For Total or Total Dissolved Fluoride, the Bellack distillation is required for NPDES monitoring but is not required for SDWA monitoring.
2. Summary of Method
 - 2.1 The fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.
 - 2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl⁻(0.3), F⁻(0.001) LaF/test solution/SCE/.
3. Interferences
 - 3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si⁴⁺, Fe³⁺ and Al³⁺ interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon and iron and eliminates the pH problem.
4. Sampling Handling and Preservation
 - 4.1 No special requirements.
5. Apparatus
 - 5.1 Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.
 - 5.2 Fluoride Ion Activity Electrode, such as Orion No. 94-09⁽¹⁾.
 - 5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.
 - 5.4 Magnetic Mixer, Teflon-coated stirring bar.

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6. Reagents

- 6.1 Buffer solution, pH 5.0–5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 4 g of CDTA⁽²⁾. Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.
- 6.2 Sodium fluoride, stock solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.
- 6.3 Sodium fluoride, standard solution: 1.0 ml = 0.01 mg F. Dilute 100.0 ml of sodium fluoride stock solution (6.2) to 1000 ml with distilled water.
- 6.4 Sodium hydroxide, 5N: Dissolve 200 g sodium hydroxide in distilled water, cool and dilute to 1 liter.

7. Calibration

- 7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/l by diluting appropriate volumes to 50.0 ml. The following series may be used:

Millimeters of Standard (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

- 7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

- 8.1 Place 50.0 ml of sample or standard solution and 50.0 ml of buffer (See Note) in a 150 ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential

reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/l on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (> 9), add 1 N HCl to adjust pH to 8.3.

9. Precision and Accuracy

- 9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/l fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/l with a standard deviation of ± 0.03 was obtained.
- 9.2 On the same study, a synthetic sample containing 0.75 mg/l fluoride, 2.5 mg/l polyphosphate and 300 mg/l alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/l fluoride with a standard deviation of ± 0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid. (The monohydrate form may also be used.) Eastman Kodak 15411, Mallinckrodt 2357, Sigma D 1383, Tridom-Fluka 32869-32870 or equivalent.
3. Standard Methods for the Examination of Water and Wastewaters, p 389, Method No. 414A, Preliminary Distillation Step (Bellack), and p 391, Method No. 414B, Electrode Method, 14th Edition (1975).
4. Annual Book of ASTM Standards, Part 31, "Water", Standard D1179-72, Method B, p 312 (1976).

METHOD 1110

CORROSIVITY TOWARD STEEL

1.0 SCOPE AND APPLICATION

1.1 Method 1110 is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

2.0 SUMMARY OF METHOD

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

3.0 INTERFERENCES

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within 10%. However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

4.0 APPARATUS AND MATERIALS

4.1 An apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5,000 mL), a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type of test is shown in Figure 1.

4.2 The supporting device and container shall be constructed of materials that are not affected by, or cause contamination of, the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test, but it should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon, or coated metal.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

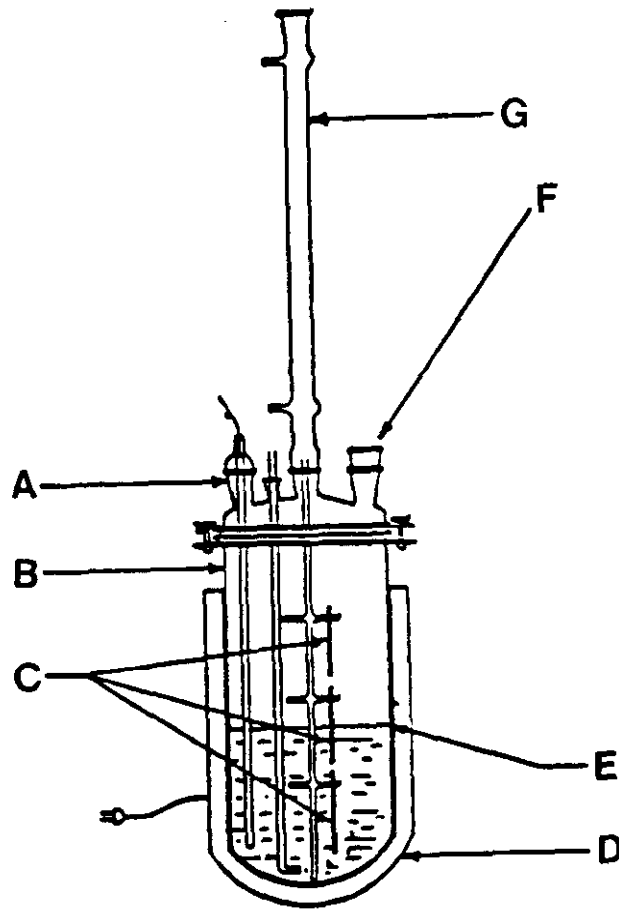


Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = heating mantle, E = liquid interface, F = opening in flask for additional apparatus that may be required, and G = reflux condenser.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 in.) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 in.) and a 0.80-cm (0.4-in.)-diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2 - d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where:

t = thickness.

D = diameter of the specimen.

d = diameter of the mounting hole.

If the hole is completely covered by the mounting support, the last term in the equation, $(t)(3.14)(d)$, is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to $\pm 1\%$ is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished by chemical treatment (pickling), by electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 in.) or 2-3 mg/cm² should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleach-free scouring powder, followed by rinsing in distilled water and then in acetone or methanol, and finally by air-drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 mL/cm².

5.0 REAGENTS

5.1 Sodium hydroxide (NaOH), (20%): Dissolves 200 g NaOH in 800 mL Type II water and mix well.

5.2 Zinc dust.

5.3 Hydrochloric acid (HCl): Concentrated.

5.4 Stannous chloride (SnCl₂).

5.5 Antimony chloride (SbCl₃).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Assemble the test apparatus as described in Paragraph 4.0, above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device, bring the temperature of the waste to 55°C (130°F).

7.5 An accurate rate of corrosion is not required; only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year is required. A 24-hr test period should be ample to determine whether or not the rate of corrosion is >6.35 mm per year.

7.6 In order to determine accurately the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease, or resinous materials and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

<u>Solution</u>	<u>Soaking Time</u>	<u>Temperature</u>
20% NaOH + 200 g/L zinc dust	5 min	Boiling
or		
Conc. HCl + 50 g/L SnCl ₂ + 20 g/L SbCl ₃	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed uses:

Solution:	50 g/L H ₂ SO ₄
Anode:	Carbon or lead
Cathode:	Steel coupon
Cathode current density:	20 amp/cm ² (129 amp/in. ²)
Inhibitor:	2 cc organic inhibitor/liter
Temperature:	74°C (165°F)
Exposure Period:	3 min.

NOTE: Precautions must be taken to ensure good electrical contact with the coupon to avoid contamination of the cleaning solution with easily reducible metal ions and to ensure that inhibitor decomposition has not occurred. Instead of a proprietary inhibitor, 0.5 g/L of either diorthotolyl thiourea or quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined by using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighed. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss} \times 11.145}{\text{area} \times \text{time}}$$

where: weight loss is in milligrams,
area in square centimeters,
time in hours, and
corrosion rate in millimeters per year (mmpy).

8.0 QUALITY CONTROL

8.1 All quality control data should be filed and available for auditing.

8.2 Duplicate samples should be analyzed on a routine basis.

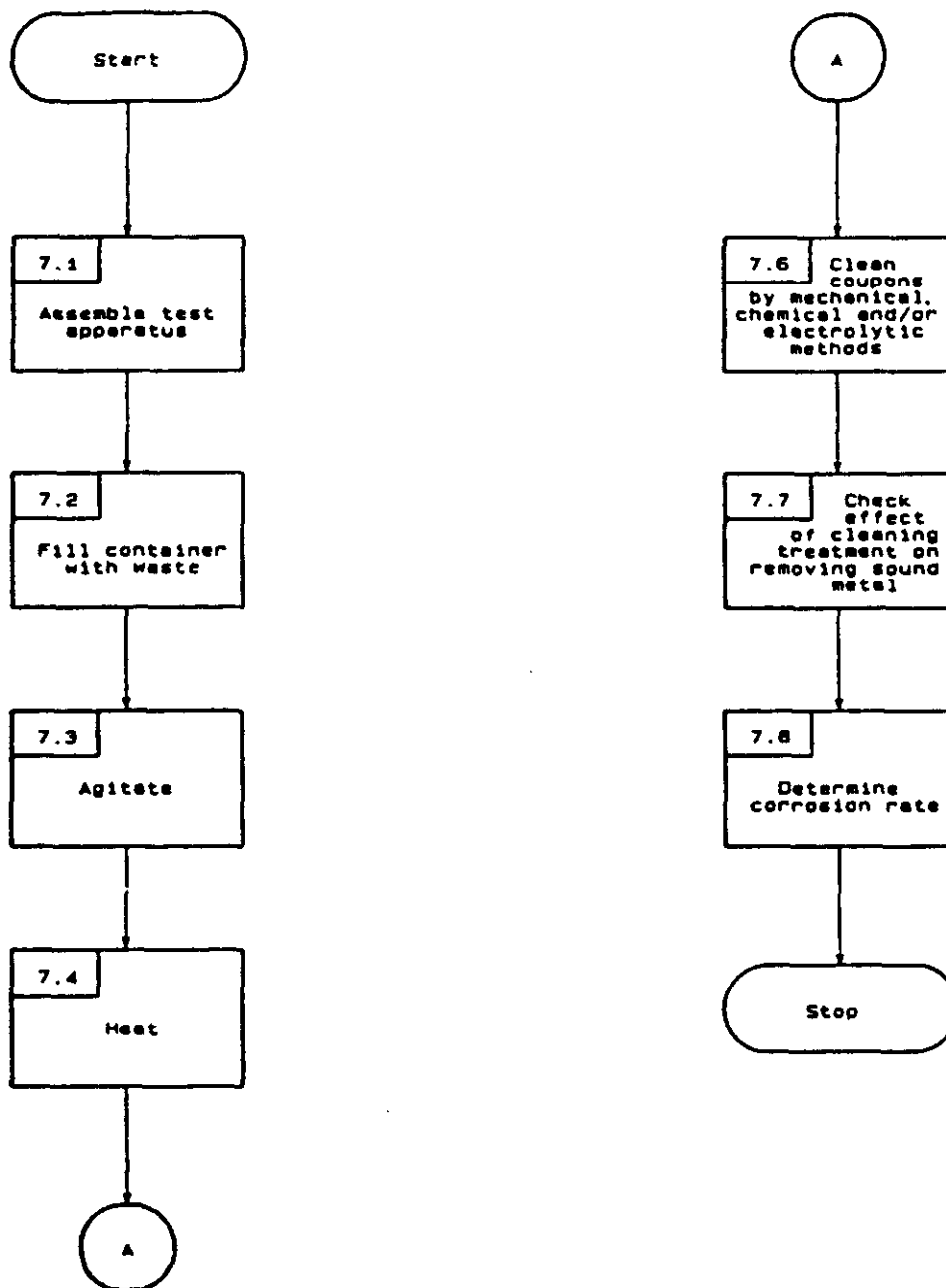
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. National Association of Corrosion Engineers, "Laboratory Corrosion Testing of Metals for the Process Industries," NACE Standard TM-01-69 (1972 Revision), NACE, 3400 West Loop South, Houston, TX 77027.

METHOD 1110
CORROSIVITY TOWARD STEEL



METHOD 9045

SOIL pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure which has been approved for measuring pH in calcareous and noncalcareous soils.

2.0 SUMMARY OF METHOD

2.1 The soil sample is mixed either with Type II water or with a calcium chloride solution (see Section 5.0), depending on whether the soil is considered calcareous or noncalcareous. The pH of the solution is then measured with a pH meter.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10 , the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1 , may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can either (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Electrodes:

4.2.1 Calomel electrode.

4.2.2 Glass electrode.

4.2.3 A combination electrode can be employed instead of calomel or glass.

4.5 Beaker: 50-mL.

4.6 Volumetric flask: 2-Liter.

4.7 Volumetric flask: 1-Liter.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Primary standard buffer salts are available from the National Bureau of Standards (NBS) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NBS salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NBS standards, are recommended for routine use.

5.4 Stock calcium chloride solution (CaCl_2), 3.6 M: Dissolve 1059 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in Type II water in a 2-liter volumetric flask. Cool the solution, dilute it to volume with Type II water, and mix it well. Dilute 20 mL of this solution to 1 liter with Type II water in a volumetric flask and standardize it by titrating a 25-mL aliquot of the diluted solution with standard 0.1 N AgNO_3 , using 1 mL of 5% K_2CrO_4 as the indicator.

5.5 Calcium chloride (CaCl_2), 0.01 M: Dilute 50 mL of stock 3.6 M CaCl_2 to 18 liters with Type II water. If the pH of this solution is not between 5 and 6.5, adjust the pH by adding a little $\text{Ca}(\text{OH})_2$ or HCl . As a check on the preparation of this solution, measure its electrical conductivity. The specific conductivity should be 2.32 ± 0.08 mmho per cm at 25°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Sample preparation and pH measurement of noncalcareous soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of Type II water and stir the suspension several times during the next 30 min.

7.2.2 Let the soil suspension stand for about 1 hr to allow most of the suspended clay to settle out from the suspension.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.5 Report the results as "soil pH measured in water."

7.3 Sample preparation and pH measurement of calcareous soils:

7.3.1 To 10 g of soil in a 50-mL beaker, add 20 mL of 0.01 M CaCl_2 (Step 5.5) solution and stir the suspension several times during the next 30 min.

7.3.2 Let the soil suspension stand for about 30 min to allow most of the suspended clay to settle out from the suspension.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed well into the partly settled suspension and the calomel electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "soil pH measured in 0.01 M CaCl_2 ".

8.0 QUALITY CONTROL

8.1 Duplicate samples and check standards should be analyzed routinely.

8.2 Electrodes must be thoroughly rinsed between samples.

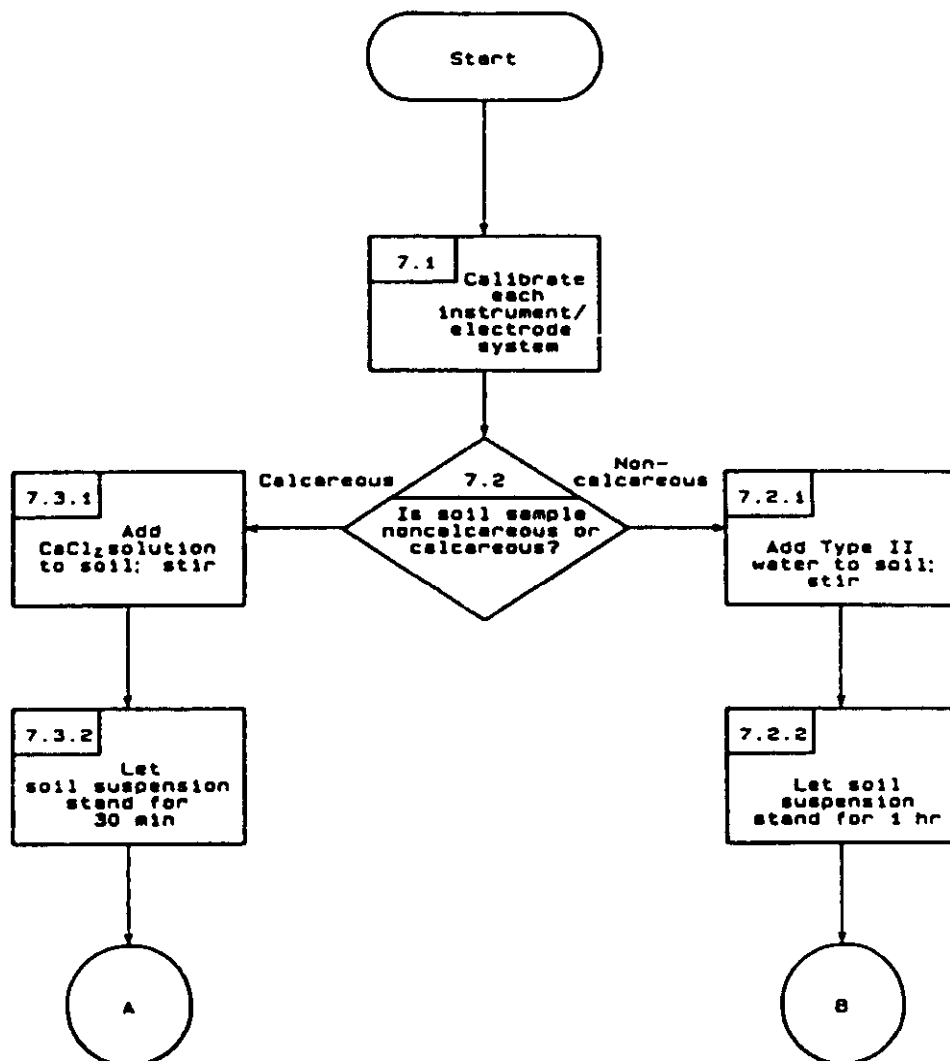
9.0 METHOD PERFORMANCE

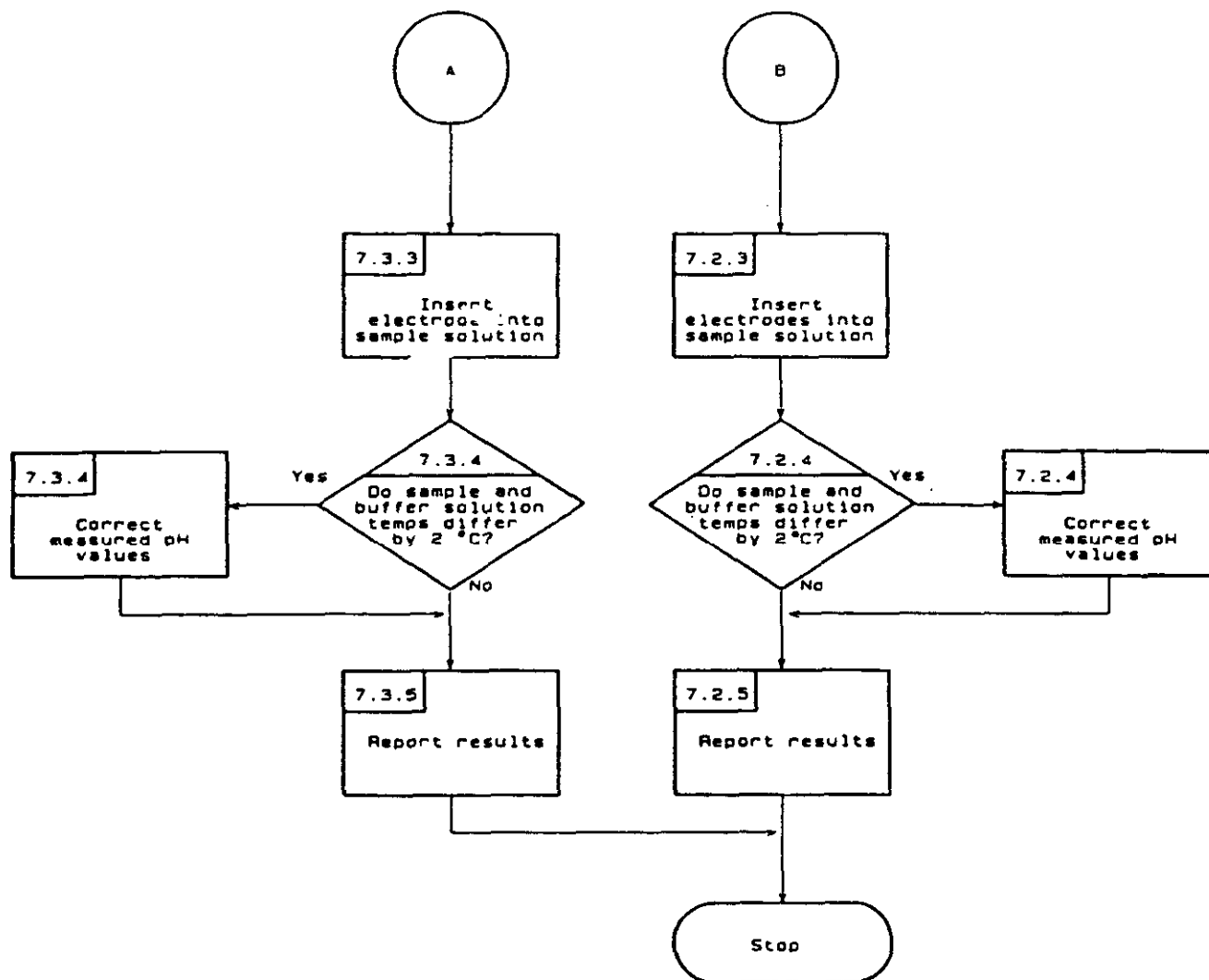
9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 9045
SOIL pH





METHOD 7060

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 1 ug/L.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background

correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using D₂ arc background correction. Zeeman background correction is very useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker: 250 mL.

4.2 Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 μ L, as required.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H₂O₂ is <MDL, the acid can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As_2O_3 , analytical reagent grade) or equivalent in 100 mL of Type II water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3 , 2 mL of 30% H_2O_2 , and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after every 10 injections of samples. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased samples must be appropriately qualified (e.g., 5 ug/g aqueous phase).

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for this method is 5-100 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

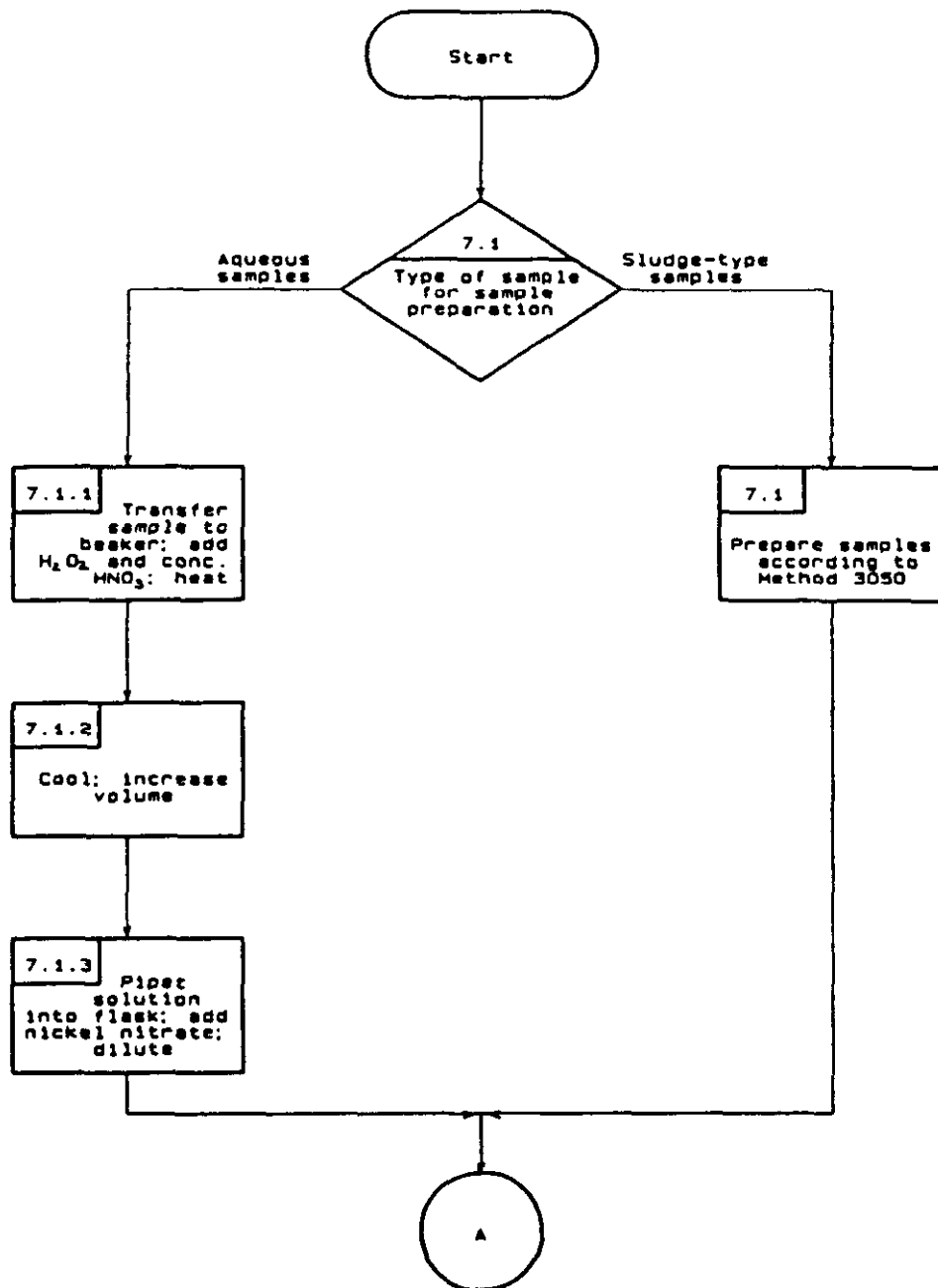
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

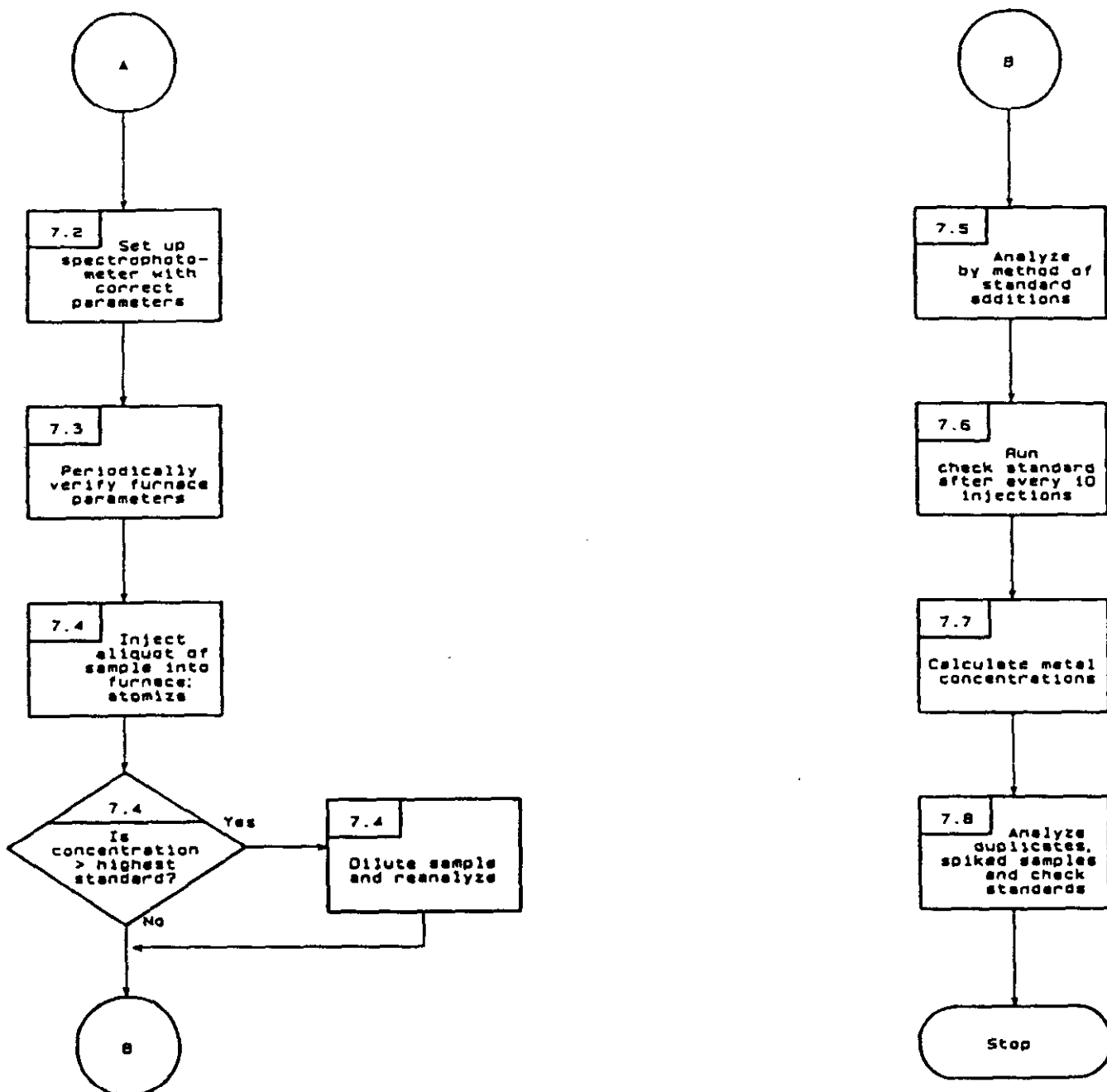
Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Oilly soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g ^a
Emission control dust	3050	430, 350 ug/g

^aBias of -30 and -28% from expected, respectively.

METHOD 7060
ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7060
ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)
(Continued)



METHOD 7080

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High hollow cathode current settings and a narrow spectral band pass must be used, because both barium and calcium emit strongly at barium's analytical wavelength.

3.3 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain 2 mL of the KCl ionization suppressant (Section 5.2.3 below) per 100 mL of solution.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

- 4.2.1 Barium hollow cathode lamp.
- 4.2.2 Wavelength: 553.6 nm.
- 4.2.3 Fuel: Acetylene.
- 4.2.4 Oxidant: Nitrous oxide.
- 4.2.5 Type of flame: Fuel rich.
- 4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.7787 g barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, analytical reagent grade in Type II water and dilute to

1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. All calibration standards and samples should contain 2 mL/100 mL of the potassium chloride (ionization suppressant) solution described in Section 5.2.3.

5.2.3 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 553.6 nm.

Sensitivity: 0.4 mg/L.

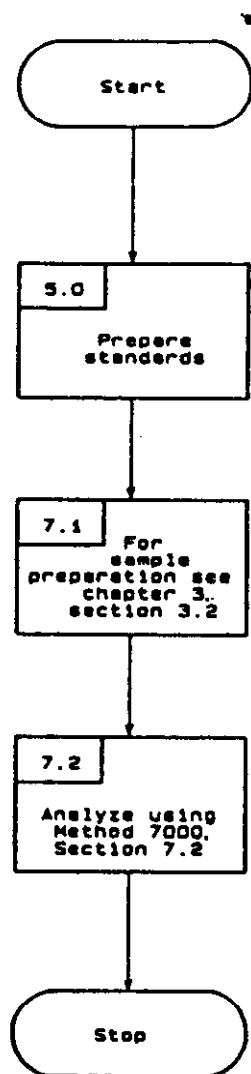
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.4 and 2 mg Ba/L gave standard deviations of ± 0.043 and ± 0.13 , respectively. Recoveries at these levels were 94% and 113%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 208.1.

METHOD 7080
BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7130

CADMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Nonspecific absorption and light scattering can be significant at the analytical wavelength. Thus background correction is required.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

- 4.2.1 Cadmium hollow cathode lamp.
- 4.2.2 Wavelength: 228.8 nm.
- 4.2.3 Fuel: Acetylene.
- 4.2.4 Oxidant: Air.
- 4.2.5 Type of flame: Oxidizing (fuel lean).
- 4.2.6 Background correction: Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.000 g cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same

concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.05-2 mg/L with a wavelength of 228.8 nm.

Sensitivity: 0.025 mg/L.

Detection limit: 0.005 mg/L.

9.2 For concentrations of cadmium below 0.02 mg/L, the furnace procedure (Method 7131) is recommended.

9.3 Precision and accuracy data are available in Method 213.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

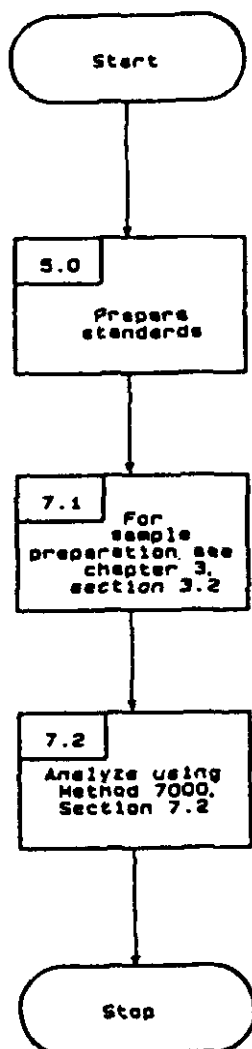
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	2,770, 1,590 ug/g
Wastewater treatment sludge	3050	12,000, 13,000 ug/g

METHOD 7130
CADMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 9252

CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to ground water, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 mL is used.

1.3 Automated titration may be used.

2.0 SUMMARY OF METHOD

2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

3.0 INTERFERENCES

3.1 Anions and cations at concentrations normally found in surface waters do not interfere. However, at the higher concentration often found in certain wastes, problems may occur.

3.2 Sulfite interference can be eliminated by oxidizing the 50 mL of sample solution with 0.5-1 mL of H_2O_2 .

4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1-mL or 5-mL microburet with 0.01-mL gradations.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Standard sodium chloride solution, 0.025 N: Dissolve 1.4613 g + 0.0002 g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1-liter volumetric flask and dilute to the mark.

5.3 Nitric acid (HNO_3) solution: Add 3.0 mL concentrated nitric acid to 997 mL of Type II water ("3 + 997" solution).

5.4 Sodium hydroxide (NaOH) solution (10 g/L): Dissolve approximately 10 g of NaOH in Type II water and dilute to 1 L.

5.5 Hydrogen peroxide (H₂O₂): 30%.

5.6 Hydroquinone solution (10 g/L): Dissolve 1 g of purified hydroquinone in water in a 100-mL volumetric flask and dilute to the mark.

5.7 Mercuric nitrate titrant (0.141 N): Dissolve 24.2 g Hg(NO₃)₂·H₂O in 900 mL of Type II water acidified with 5.0 mL concentrated HNO₃ in a 1-liter volumetric flask and dilute to the mark with Type II water. Filter, if necessary. Standardize against standard sodium chloride solution (Paragraph 5.2) using the procedures outlined in Section 7.0. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00-mL aliquot is equivalent to 5.00 mg of chloride.

5.8 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g Hg(NO₃)₂·H₂O in 50 mL of Type II water acidified with 0.05 mL of concentrated HNO₃ (sp. gr. 1.42) in a 1-liter volumetric flask and dilute to the mark with Type II water. Filter, if necessary. Standardize against standard sodium chloride solution (Paragraph 5.2) using the procedures outlined in Section 7.0. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.9 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g Hg(NO₃)₂·H₂O in 25 mL of Type II water acidified with 0.25 mL of concentrated HNO₃ (sp. gr. 1.42) in a 1-liter volumetric flask and dilute to the mark with Type II water. Filter, if necessary. Standardize against standard sodium chloride solution (Paragraph 5.2) using the procedures outlined in Section 7.0. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1-mL aliquot is equivalent to 500 ug of chloride.

5.10 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 mL 95% ethanol in a 100-mL volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 mo.

5.11 Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in 100-mL volumetric flask and dilute to the mark with 95% ethanol or isopropanol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 There are no special requirements for preservation.

7.0 PROCEDURE

7.1 Place 50 mL of sample in a vessel for titration. If the concentration is greater than 20 mg/L chloride, use 0.141 N mercuric nitrate titrant (Paragraph 5.7) in Step 7.6, or dilute sample with Type II water. If the concentration is less than 2.5 mg/L of chloride, use 0.0141 N mercuric nitrate titrant (Paragraph 5.9) in step 7.6. Using a 1-mL or 5-mL microburet, determine an indicator blank on 50 mL chloride-free water using step 7.6. If the concentration is less than 0.1 mg/L of chloride, concentrate an appropriate volume to 50 mL.

7.2 Add 5 to 10 drops of mixed indicator reagent (Paragraph 5.10); shake or swirl solution.

7.3 If a blue-violet or red color appears, add HNO_3 solution (Paragraph 5.3) dropwise until the color changes to yellow.

7.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.3) dropwise until the color changes to blue-violet; then add HNO_3 solution (5.2) dropwise until the color changes to yellow.

7.5 Add 1 mL excess HNO_3 solution (5.2).

7.6 Titrate with 0.025 N mercuric nitrate titrant (5.8) until a blue-violet color persists throughout the solution. If volume of titrant exceeds 10 mL or is less than 1 mL, use the 0.141 N or 0.0141 N mercuric nitrate solutions, respectively. If necessary, take a small sample aliquot. Alphazurine indicator solution (Paragraph 5.11) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

7.6.1 If chromate is present at <100 mg/L and iron is not present, add 5-10 drops of alphazurine indicator solution (Paragraph 5.11) and acidify to a pH of 3 (indicating paper). End point will then be an olive-purple color.

7.6.2 If chromate is present at >100 mg/L and iron is not present, add 2 mL of fresh hydroquinone solution (Paragraph 5.6).

7.6.3 If ferric iron is present use a volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 mL fresh hydroquinone solution (Paragraph 5.6).

7.6.4 If sulfite ion is present, add 0.5 mL of H_2O_2 solution (5.5) to 50-mL sample and mix for 1 min.

7.7 Calculation:

$$\text{mg chloride/liter} = \frac{(A - B)N \times 35,450}{\text{mL of sample}}$$

where:

A = mL titrant for sample;

B = mL titrant for blank; and

N = normality of mercuric nitrate titrant.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.5 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 METHOD PERFORMANCE

9.1 Forty-two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as Chloride (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as	
		Bias (%)	Bias (mg/L)
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

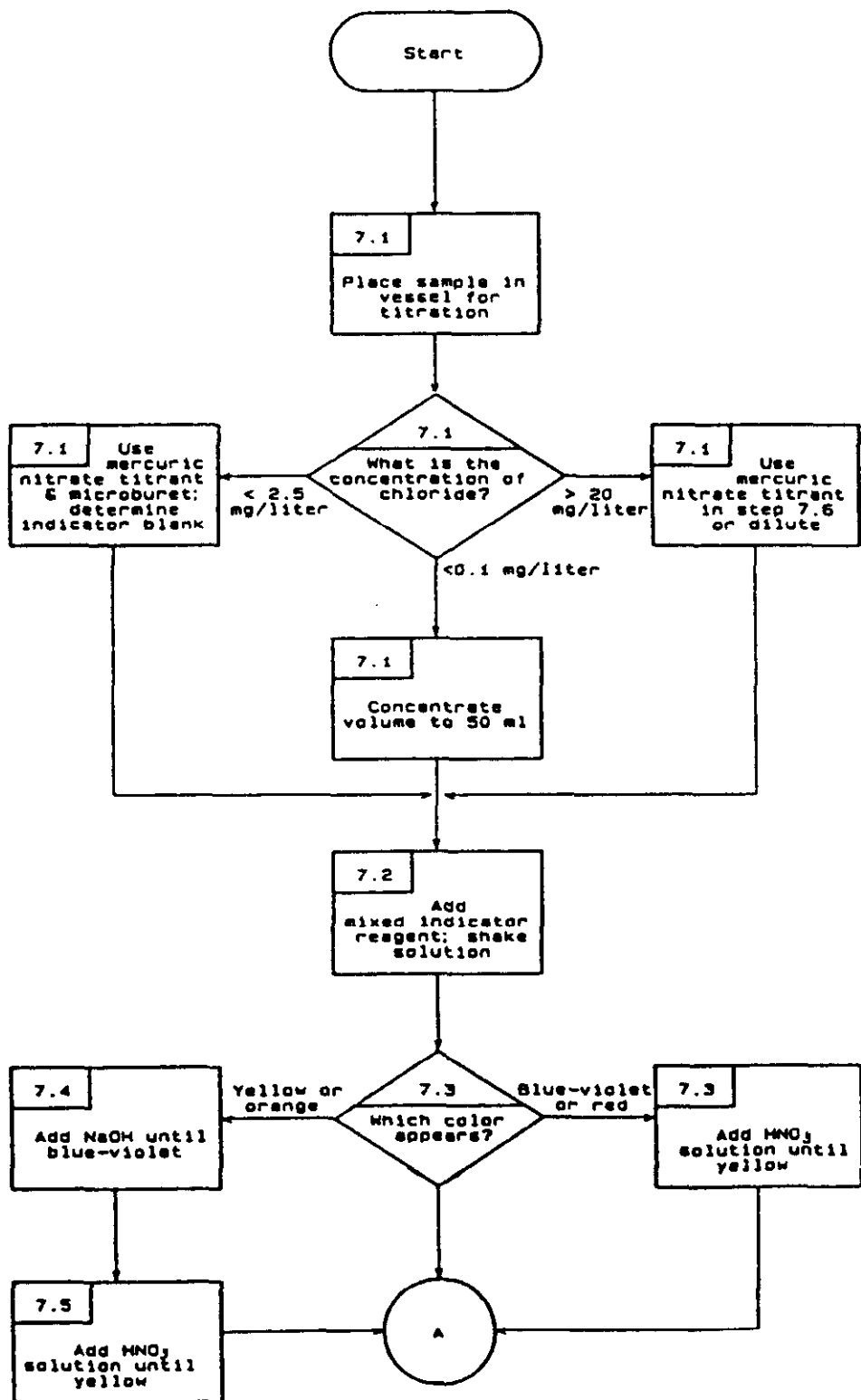
9.2 In a single laboratory, using surface water samples at an average concentration of 34 mg Cl/L, the standard deviation was ± 1.0 .

9.3 A synthetic unknown sample containing 241 mg/L chloride, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L nitrate N, 0.25 mg/L nitrate N, 259 mg/L sulfate and 42.5 mg/L total alkalinity (contributed by NaHCO_3) in Type II water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

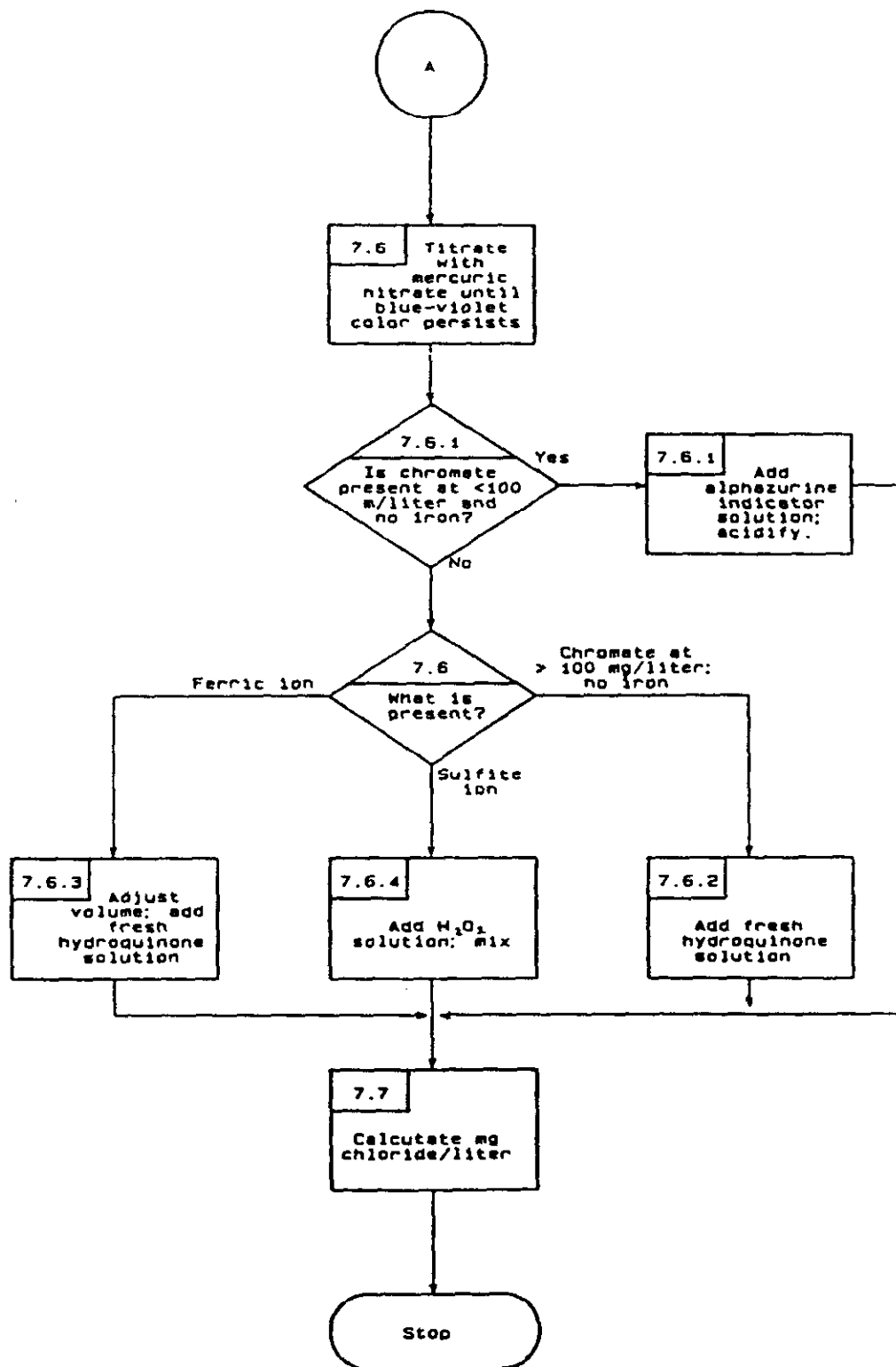
10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D512-67, Method A, p. 270 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 15th ed., (1980).
3. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020 (1983), Method 325.3.

METHOD 9252
CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)



METHOD 9252
CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)
(Continued)



METHOD 7191

CHROMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Low concentrations of calcium and/or phosphate may cause interferences; at concentrations above 200 mg/L, calcium's effect is constant and eliminates the effect of phosphate. Calcium nitrate is therefore added to ensure a known constant effect.

3.3 Nitrogen should not be used as the purge gas because of a possible CN band interference.

3.4 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 1000°C.

4.2.3 Atomizing time and temp: 10 sec at 2700°C.

4.2.4 Purge gas: Argon (nitrogen should not be used).

4.2.5 Wavelength: 357.9 nm.

4.2.6 Background correction: Not required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20- μ L injection,

continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.923 g of chromium trioxide (CrO_3 , analytical reagent grade) in Type II water, acidify with redistilled HNO_3 , and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These standards should be prepared to contain 0.5% (v/v) HNO_3 ; 1 mL of 30% H_2O_2 and 1 mL of calcium nitrate solution, Section 5.2.3, may be added to lessen interferences (see Section 3.0).

5.2.3 **Calcium nitrate solution:** Dissolve 11.8 g of calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical reagent grade), in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.2.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

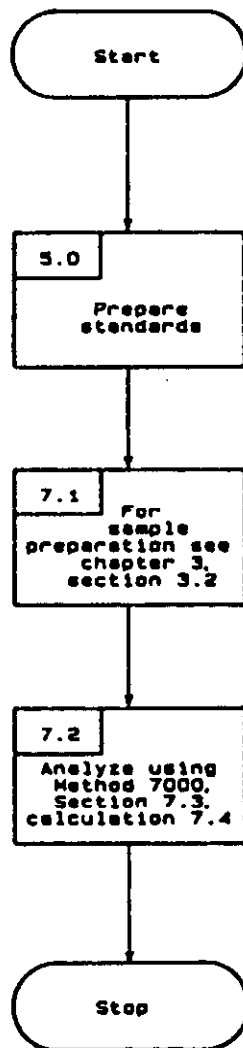
Sample Matrix	Preparation Method	Laboratory Replicates
Paint primer	3050	2.7, 2.8 mg/g
Contaminated soil	3050	12.0, 12.3 ug/g
Oilly lagoon soil	3050	69.6, 70.3 ug/g
NBS SRM 1646 Estuarine sediment	3050	42, 47 ug/g ^a
EPA QC Sludge	3050	156 ug/g ^b
NBS SRM 1085, Wear Metals in lubricating oil	3050	311, 356 ug/g ^c

^aBias of -45 and -38% from expected, respectively.

^bBias of -24% from expected.

^cBias of +4 and +19% from expected, respectively.

METHOD 7191
CHROMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7210

COPPER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Copper hollow cathode lamp.

4.2.2 Wavelength: 324.7 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background correction: Recommended, if possible.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.00 g of electrolytic copper (analytical reagent grade) in 5 mL of redistilled HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-5 mg/L with a wavelength of 324.7 nm.

Sensitivity: 0.1 mg/L.

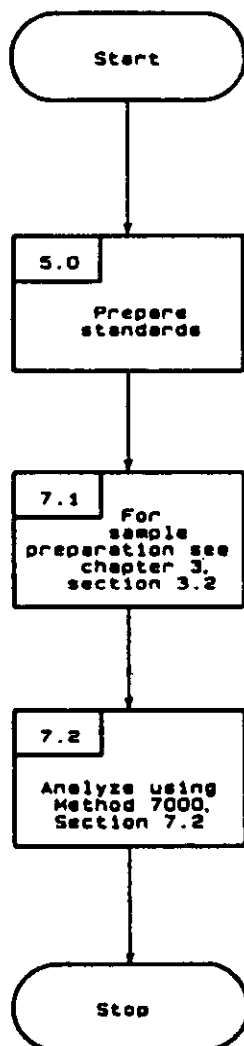
Detection limit: 0.02 mg/L.

9.2 Precision and accuracy data are available in Method 220.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 220.1.

METHOD 7210
COPPER (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7380

IRON (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Iron is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Iron hollow cathode lamp.

4.2.2 Wavelength: 248.3 nm (primary); 248.8, 271.9, 302.1, 252.7, or 372.0 nm (alternates).

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background correction: Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.000 g iron wire (analytical reagent grade) in 10 mL redistilled HNO_3 and Type II water and dilute to 1 liter with Type II water. Note that iron passivates in concentrated HNO_3 , and thus some water should be present. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3-5 mg/L with a wavelength of 248.3 nm.

Sensitivity: 0.12 mg/L.

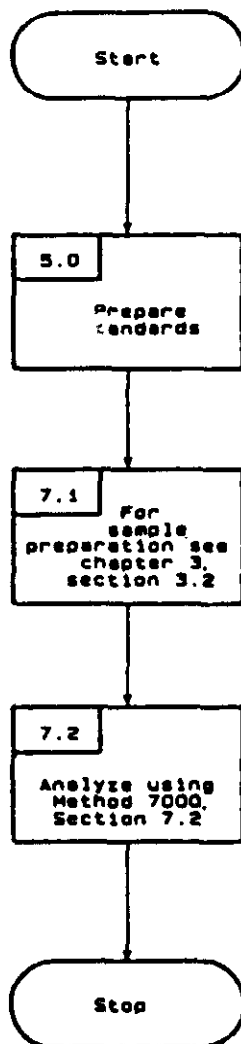
Detection limit: 0.03 mg/L.

9.2 Precision and accuracy data are available in Method 236.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 236.1.

METHOD 7380
IRON (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7470

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

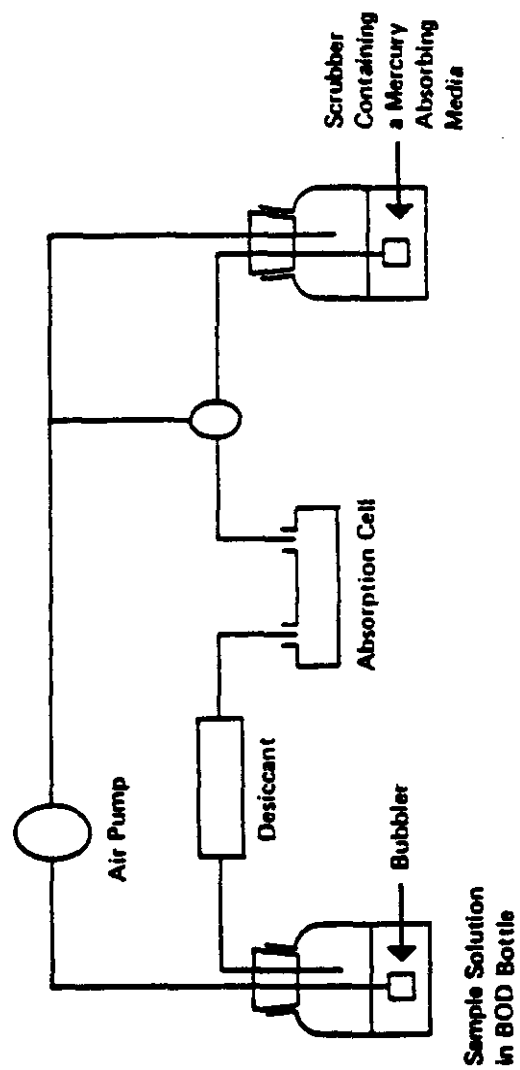


Figure 1. Apparatus for flameless mercury determination.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4 ; or
2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4 . This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 g per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH < 2 with HNO_3 . The suggested maximum holding times for these samples are 38 days in glass containers and 13 days in plastic containers.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing < 1.0 g of mercury, to a 300-mL BOD bottle. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3 , mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C . Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 μg of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of KMnO_4 solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C . Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and

continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

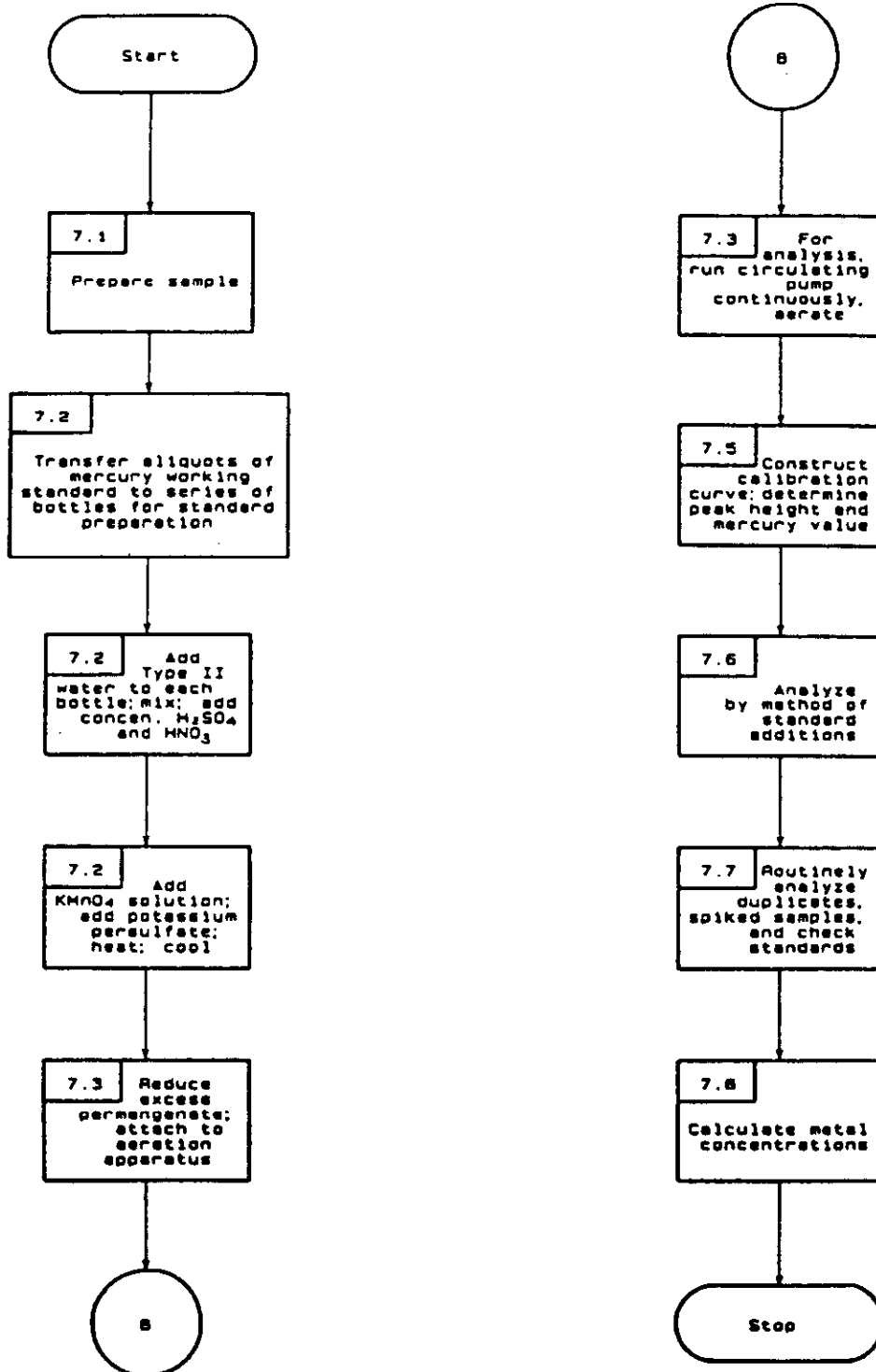
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.

METHOD 7470
MERCURY (MANUAL COLD-VAPOR TECHNIQUE)



METHOD 7610

POTASSIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In air/acetylene or other high-temperature flames ($>2800^{\circ}\text{C}$), potassium can experience partial ionization, which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization-suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1,000 $\mu\text{g/mL}$) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

- 4.2.1 Potassium hollow cathode lamp.
- 4.2.2 Wavelength: 766.5 nm.
- 4.2.3 Fuel: Acetylene.
- 4.2.4 Oxidant: Air.
- 4.2.5 Type of flame: Slightly oxidizing (fuel lean).
- 4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.907 g of potassium chloride, KCl (analytical reagent grade), dried at 110°C in Type II water and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.1-2 mg/L with a wavelength of 766.5 nm.

Sensitivity: 0.04 mg/L.

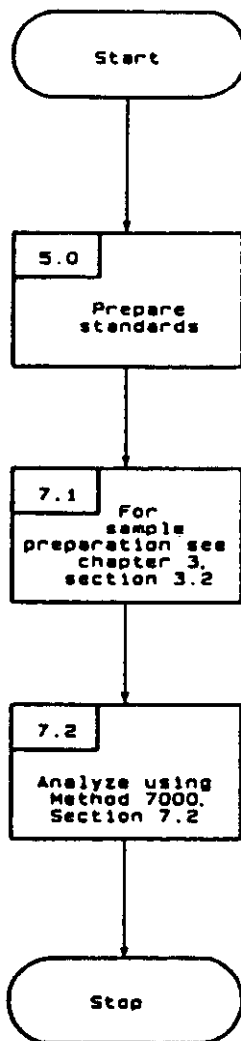
Detection limit: 0.01 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 1.6 and 6.3 mg/L gave standard deviations of ± 0.2 and ± 0.5 , respectively. Recoveries at these levels were 103% and 102%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 258.1.

METHOD 7610
POTASSIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7770

SODIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Ionization interferences can affect analysis for sodium; therefore, samples and standards must be matrix matched or an ionization suppressant employed.

3.3 Sodium is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Sodium hollow cathode lamp.

4.2.2 Wavelength: 589.6 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 2.542 g sodium chloride, NaCl (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO₃, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.03-1 mg/L with a wavelength of 589.6 nm.

Sensitivity: 0.015 mg/L.

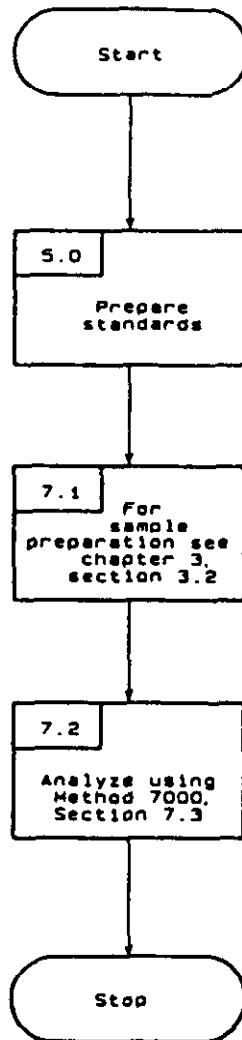
Detection limit: 0.002 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 8.2 and 52 mg/L gave standard deviations of ± 0.1 and ± 0.8 , respectively. Recoveries at these levels were 102% and 100%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 273.1.

METHOD 7770
SODIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7420

LEAD (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required at either wavelength.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Lead hollow cathode lamp.

4.2.2 Wavelength: 283.3 nm (primary); 217.0 nm (alternate).

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background correction: Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.599 g of lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO_3 , and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 283.3 nm.

Sensitivity: 0.5 mg/L.

Detection limit: 0.1 mg/L.

9.2 For concentrations of lead below 0.2 mg/L, the furnace technique (Method 7421) is recommended.

9.3 Precision and accuracy data are available in Method 239.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

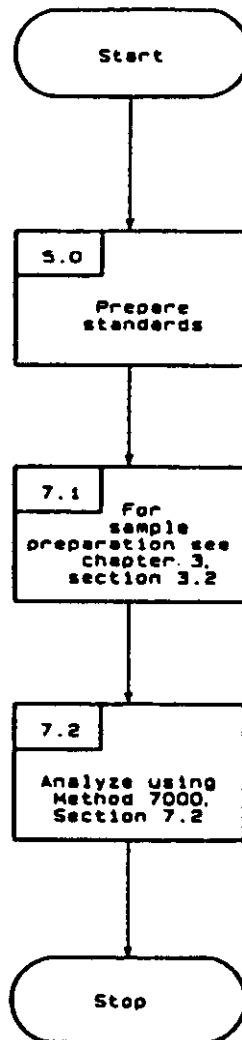
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 239.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	450, 404 ug/g
Emission control dust	3050	42,500, 63,600 ug/g

METHOD 7420
LEAD (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert samples to suitable solutions for analysis. The sample-preparation procedure varies, depending on the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 ug/L.

3.0 INTERFERENCES

3.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Zeeman background correction can be useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 APPARATUS AND MATERIALS

4.1 250-mL Griffin beaker.

4.2 10-mL volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Selenium hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for the analysis of Se.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis, such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 μ L, as required.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank made with the oxidant is <MDL, the oxidant can be used.

5.4 Selenium standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3 , analytical reagent grade) or equivalent in Type II water and dilute to 200 mL.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3 , 2 mL of 30% H_2O_2 , and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Steps 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured μL -aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be analyzed every 20 samples.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

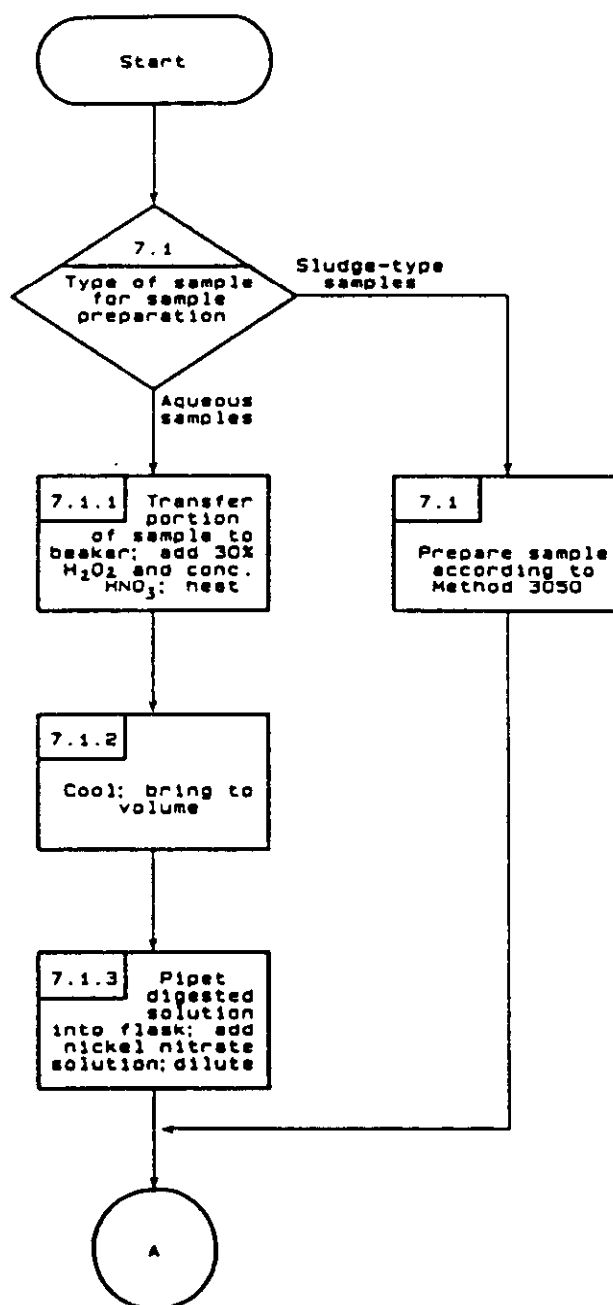
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.2.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

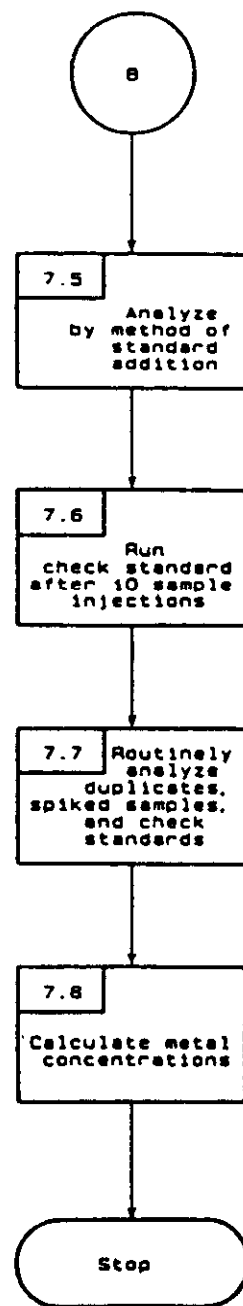
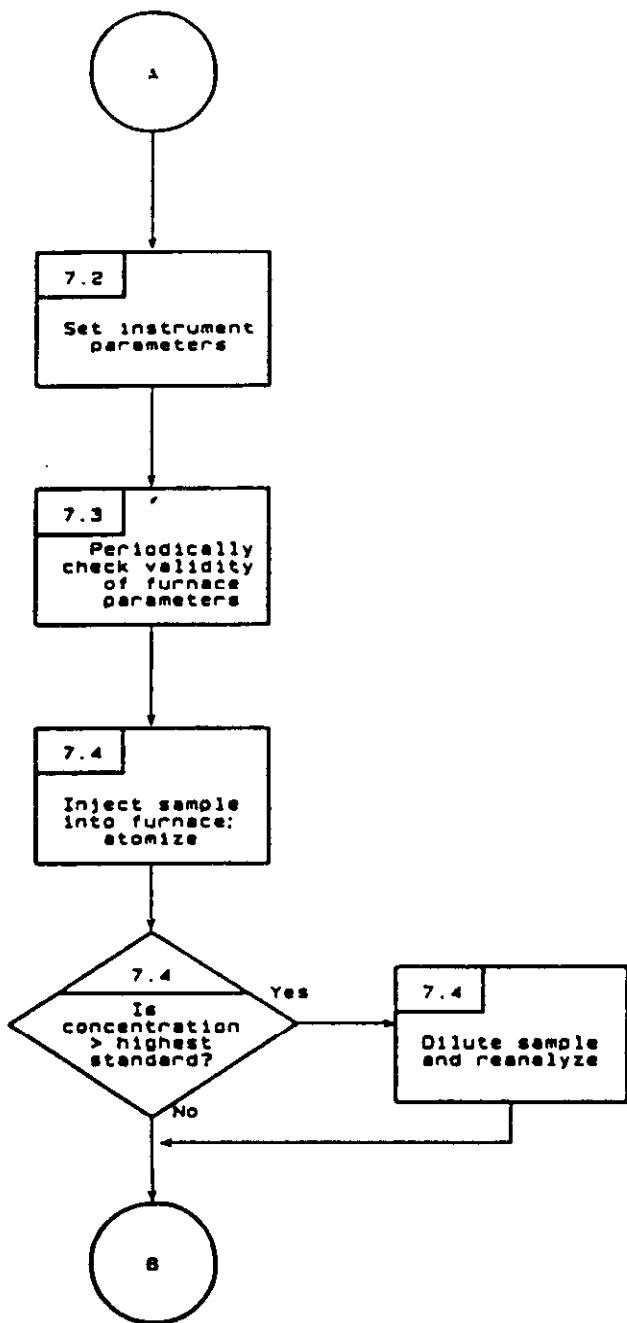
TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	14, 11 ug/g

METHOD 7740
SELENIUM (ATOMIC ABSORPTION, FURNACE METHOD)



METHOD 7740
 SELENIUM (ATOMIC ABSORPTION, FURNACE METHOD)
 (Continued)



METHOD 7760

SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/L; typical sensitivity is 0.06 mg/L.

3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Silver hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated ammonium hydroxide (NH_4OH): Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Silver standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.7874 g anhydrous silver nitrate (AgNO_3), analytical reagent grade, in Type II water. Add 5 mL concentrated HNO_3 and bring to volume in a 500-mL volumetric flask (1 mL = 1 mg Ag).

5.5 Silver working standards: These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.6 Iodine solution, 1 N: Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 mL Type II water. Add 12.7 g iodine (I_2), analytical reagent grade, and dilute to 100 mL. Place in a brown bottle.

5.7 Cyanogen iodide solution: To 50 mL Type II water add 4.0 mL concentrated NH_4OH , 6.5 g KCN, and 5.0 mL of iodine solution. Mix and dilute to 100 mL with Type II water. Do not keep longer than 2 wk.

CAUTION: This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH < 2 with nitric acid.

6.4 When possible, standards and samples should be stored in the dark and in brown bottles.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared according to Paragraphs 7.2 and 7.3. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples:

7.2.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 mL of concentrated HNO_3 . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated HNO_3 . Re-cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic types of samples.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with Type II water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample.

CAUTION: This can be done only after digestion to prevent formation of toxic cyanide under acid conditions.

If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner.

CAUTION: Cyanogen iodide must not be added to the acidified silver standards.

New standards must be made, as directed in Paragraphs 5.4 and 5.5, except that the acid addition step must be omitted. Transfer 10 mL of stock solution to a small beaker. Add Type II water to make about 80 mL. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with Type II water. Add 1 mL cyanogen iodide and allow to stand 1 hr. Transfer quantitatively to a 100-mL volumetric flask and bring to volume with Type II water.

7.4 The 328.1-nm wavelength line and background correction shall be employed.

7.5 An oxidizing air-acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.7 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances, or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

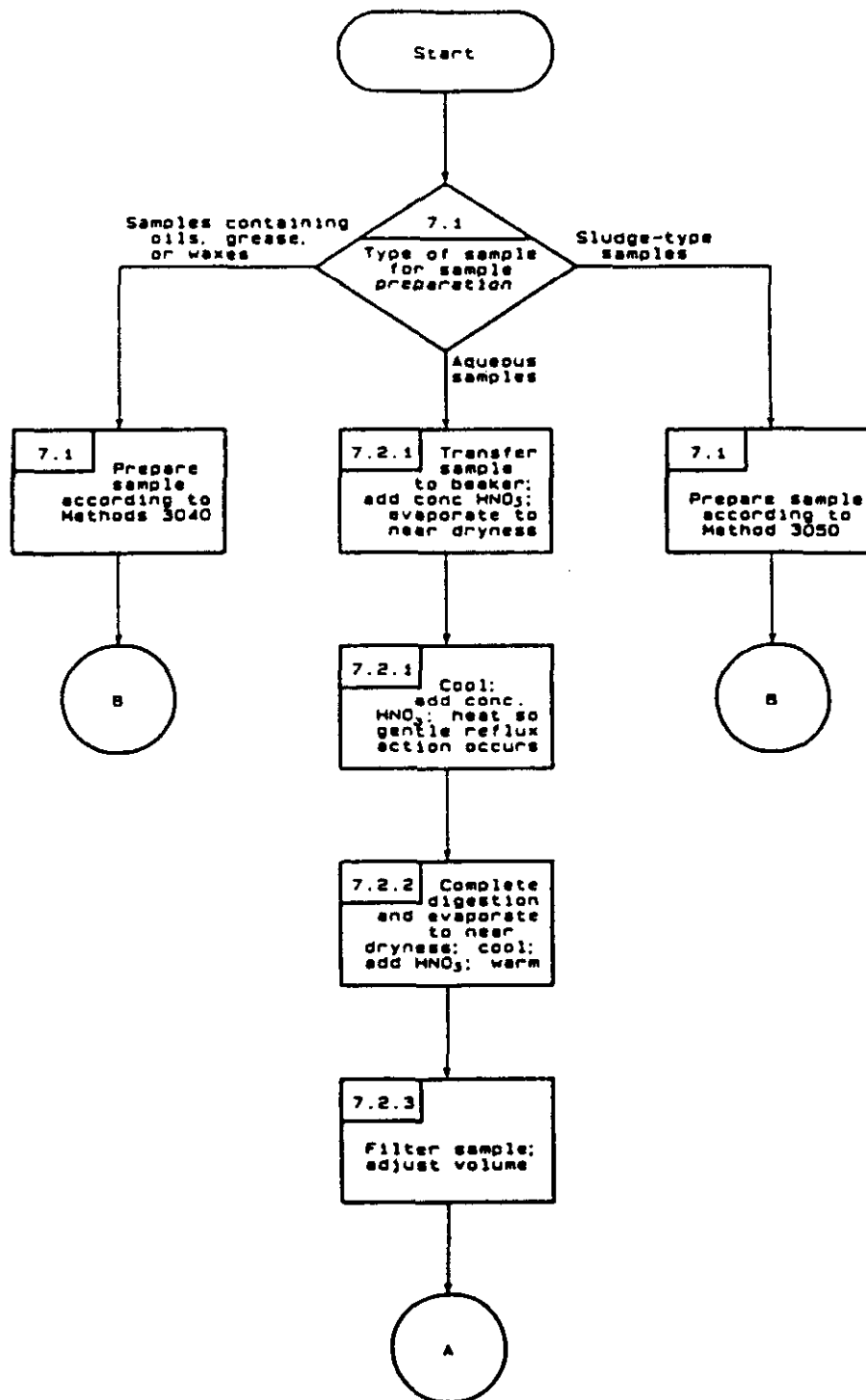
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 272.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

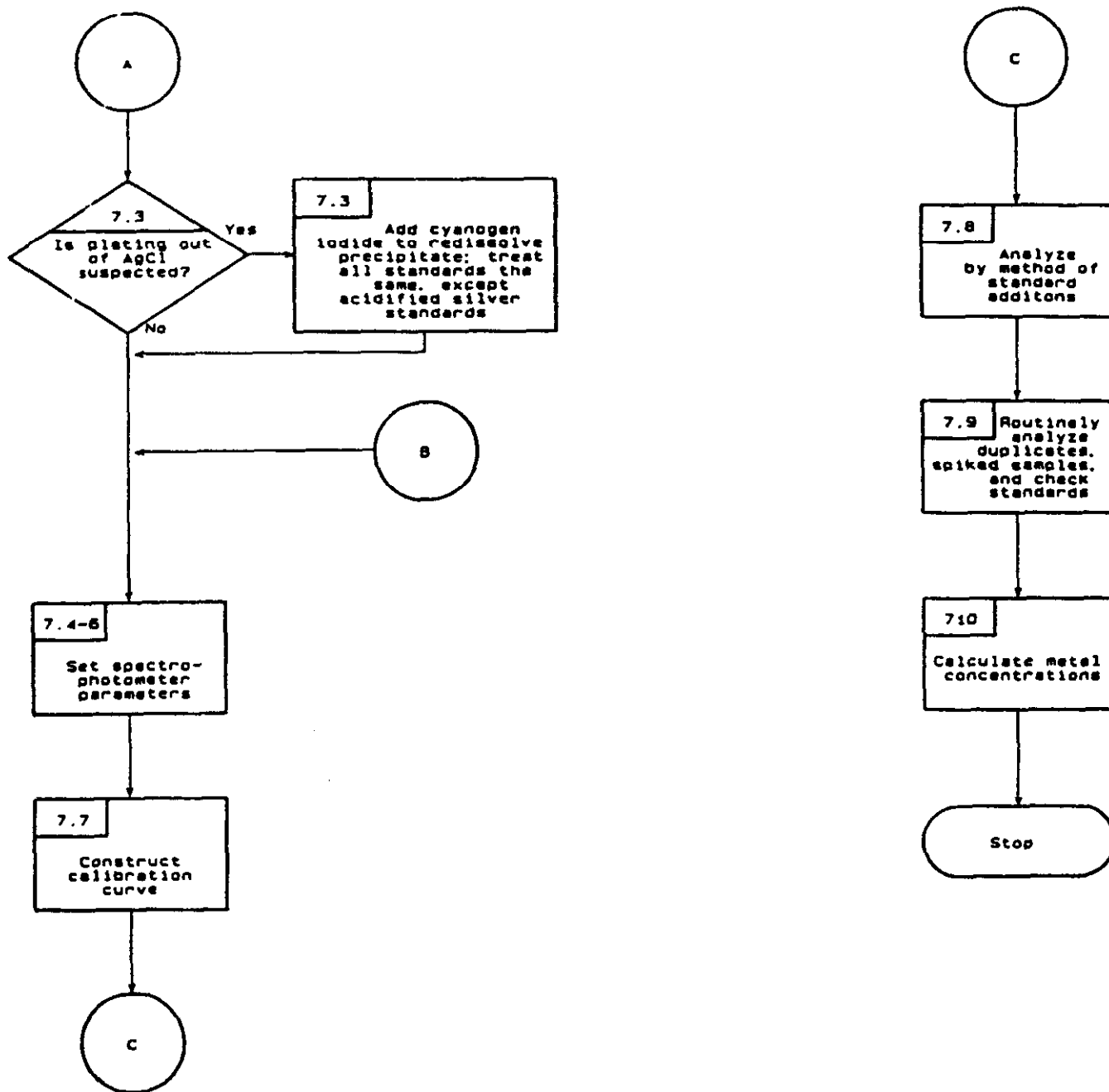
TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	2.3, 1.6 ug/g
Emission control dust	3050	1.8, 4.2 ug/g

METHOD 7760
SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)



METHOD 7760
SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)
(Continued)



METHOD 9200

NITRATE

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of ground water, drinking, surface, and saline waters, and domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

1.2 The applicable range of concentration is 0.1 to 2 mg NO₃-N per liter of sample.

2.0 SUMMARY OF METHOD

2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H₂SO₄ solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

3.0 INTERFERENCES

3.1 Dissolved organic matter will cause an off color in 13 N H₂SO₄ and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color, not due to dissolved organics, that is present.

3.2 If the sample is colored or if the conditions of the test cause extraneous coloration, this interference should be corrected by running a concurrent sample under the same conditions but in the absence of the brucine-sulfanilic acid reagent.

3.3 Strong oxidizing or reducing agents cause interference. The presence of oxidizing agents may be determined by a residual chlorine test; reducing agents may be detected with potassium permanganate.

3.3.1 Oxidizing agents' interference is eliminated by the addition of sodium arsenite.

3.3.2 Reducing agents may be oxidized by addition of H₂O₂.

3.4 Ferrous and ferric iron and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/L these are negligible.

3.5 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer or filter photometer suitable for measuring absorbance at 410 nm.

4.2 Sufficient number of 40- to 50-mL glass sample tubes for reagent blanks, standards, and samples.

4.3 Neoprene-coated wire racks to hold sample tubes.

4.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept the required number of tubes without a significant drop in temperature when the tubes are immersed.

4.5 Water bath suitable for use at 10-15°C.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sodium chloride solution (30%): Dissolve 300 g NaCl in Type II water and dilute to 1 liter.

5.3 Sulfuric acid solution: Carefully add 500 mL concentrated H₂SO₄ to 125 mL Type II water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

5.4 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate -- (C₂₃H₂₆N₂O₄)₂·H₂SO₄·7H₂O -- and 0.1 g sulfanilic acid (NH₂C₆H₄SO₃H·H₂O) in 70 mL hot Type II water. Add 3 mL concentrated HCl, cool, mix, and dilute to 100 mL with Type II water. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not affect its usefulness. Mark bottle with warning, "CAUTION: Brucine Sulfate is toxic; do not ingest."

5.5 Potassium nitrate stock solution (1.0 mL = 0.1 mg NO₃-N): Dissolve 0.7218 g anhydrous potassium nitrate (KNO₃) in Type II water and dilute to 1 liter in a volumetric flask. Preserve with 2 mL chloroform per liter. This solution is stable for at least 6 mon.

5.6 Potassium nitrate standard solution (1.0 mL = 0.001 mg NO₃-N): Dilute 10.0 mL of the stock solution (5.5) to 1 liter in a volumetric flask. This standard solution should be prepared fresh weekly.

5.7 Acetic acid (1+3): Dilute 1 volume glacial acetic acid (CH_3COOH) with 3 volumes of Type II water.

5.8 Sodium hydroxide (1 N): Dissolve 40 g of NaOH in Type II water. Cool and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Analysis should be done as soon as possible. If analysis can be done within 24 hr, the sample should be preserved by refrigeration at 4°C . When samples must be stored for more than 24 hr, they should be preserved with sulfuric acid (2 mL/L concentrated H_2SO_4) and refrigerated.

7.0 PROCEDURE

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (Paragraph 5.7) or sodium hydroxide (Paragraph 5.8). If necessary, filter to remove turbidity. Sulfuric acid can be used in place of acetic acid, if preferred.

7.2 Set up the required number of sample tubes in the rack to handle reagent blank, standards, and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, run a set of duplicate samples to which all reagents, except the brucine-sulfanilic acid, have been added.

7.3.1 Add 0.5 mL brucine-sulfanilic acid reagent (Paragraph 5.4) to each tube (except the interference control tubes) and carefully mix by swirling; then place the rack of tubes in the 100°C water bath for exactly 25 min.

CAUTION: Immersion of the tube rack into the bath should not decrease the temperature of the bath by more than $1-2^\circ\text{C}$. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.4 Pipet 10.0 mL of standards and samples or an aliquot of the samples diluted to 10.0 mL into the sample tubes.

7.5 If the samples are saline, add 2 mL of the 30% sodium chloride solution (Paragraph 5.2) to the reagent blank, standards, and samples. For freshwater samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling and place rack in cold-water bath (0-10°C).

7.6 Pipet 10.0 mL of sulfuric acid solution (Paragraph 5.3) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Remove rack of tubes from the hot-water bath, immerse in the cold-water bath, and allow to reach thermal equilibrium (20-25°C).

7.8 Read absorbance against the reagent blank at 410 nm using a 1-cm or longer cell.

7.9 Calculation:

7.9.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg/L $\text{NO}_3\text{-N}$. (The color reaction does not always follow Beer's law.)

7.9.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg/L $\text{NO}_3\text{-N}$. Multiply by an appropriate dilution factor if less than 10 mL of sample is taken.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Linear calibration curves must be composed of a minimum of a blank and five standards. A set of standards must be included with each batch of samples.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

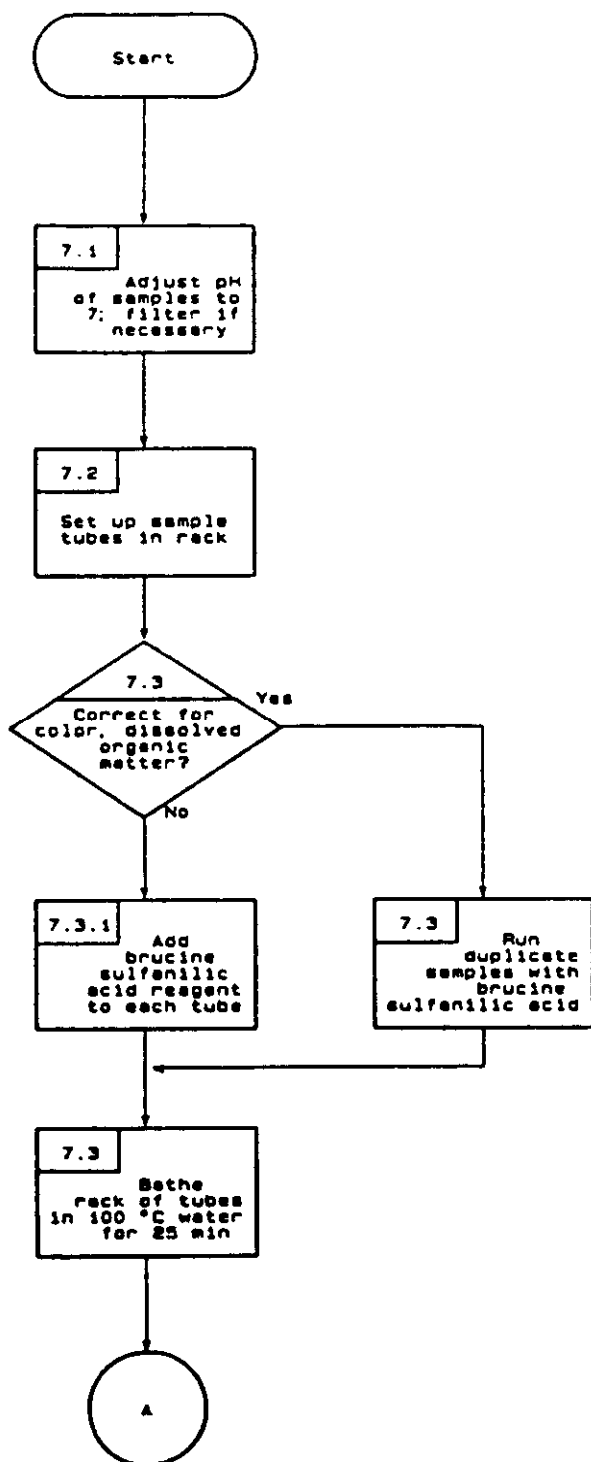
9.1 Twenty-seven analysts in fifteen laboratories analyzed natural-water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate (mg/L N)	Precision as Standard Deviation (mg/L N)	Accuracy as Bias (%)	Bias (mg/L N)
0.16	0.092	-6.79	-0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

10.0 REFERENCES

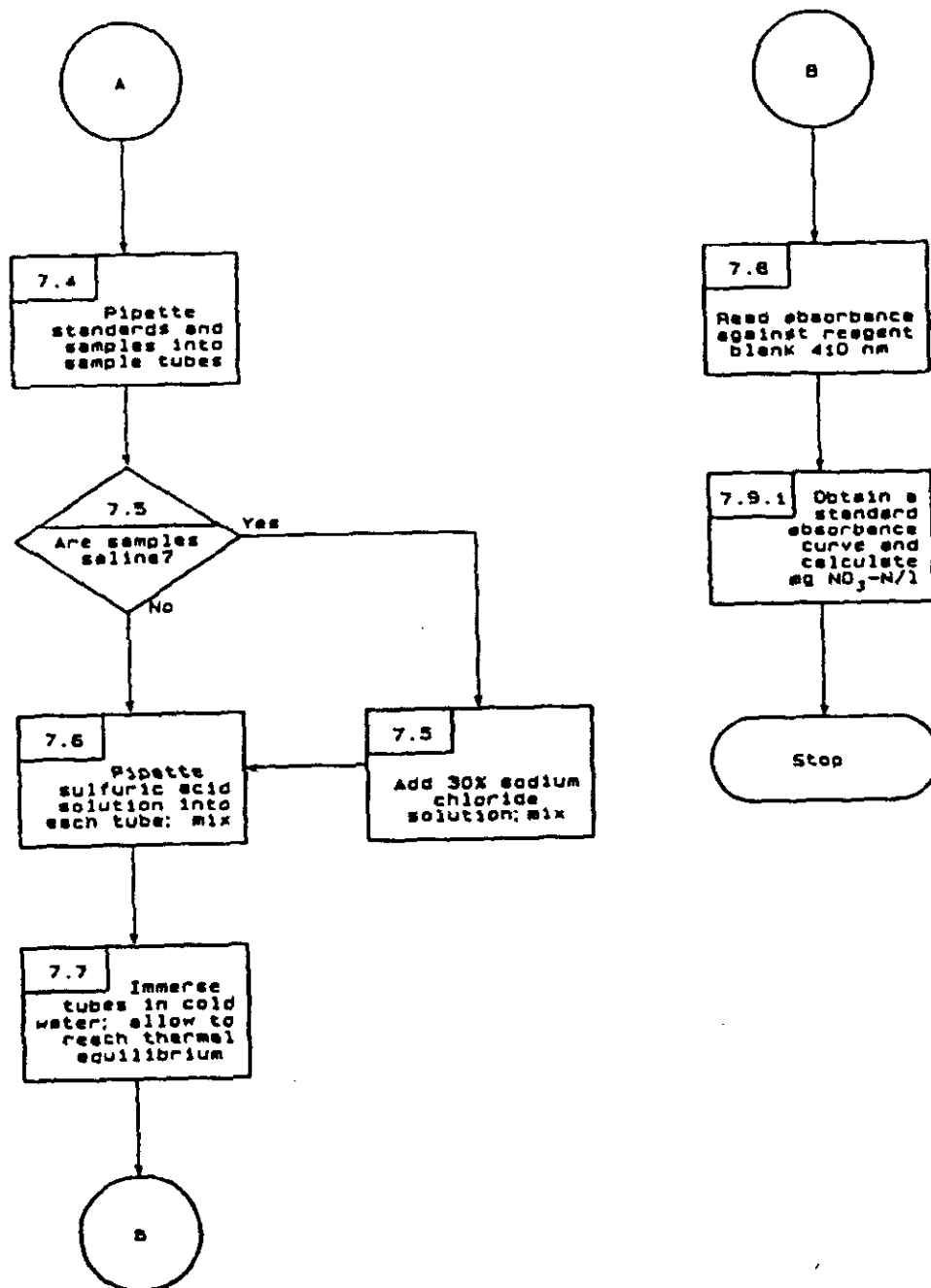
1. Annual Book of ASTM Standards, Part 31, "Water," Standard D992-71, p. 363 (1976).
2. Jenkins, D. and L. Medsken, "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine, and Fresh Water," Anal.Chem., 36, p. 610 (1964).
3. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 427, Method 419D (1975).

METHOD 9200
NITRATE



METHOD 9200

NITRATE
(Continued)



METHOD 9035

SULFATE (COLORIMETRIC, AUTOMATED, CHLORANILATE)

1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking and surface waters, and domestic and industrial wastes containing 10 to 400 mg SO_4^{-2} /liter.

2.0 SUMMARY OF METHOD

2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid solution is proportional to the amount of sulfate present.

3.0 INTERFERENCES

3.1 Cations such as calcium, aluminum, and iron interfere by precipitating the chloranilate. These ions are removed by passage through an ion-exchange column.

3.2 Samples should be centrifuged or filtered before analysis.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument, with:

4.1.1 Sampler I.

4.1.2 Continuous filter.

4.1.3 Manifold.

4.1.4 Proportioning pump.

4.1.5 Colorimeter: Equipped with 15 mm tubular flowcell and 520 nm filters.

4.1.6 Recorder.

4.1.7 Heating bath, 45°C.

4.2 Magnetic stirrer.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Barium chloranilate: Add 9 g of barium chloranilate ($\text{BaC}_6\text{Cl}_2\text{O}_4$) to 333 mL of spectrophotometric grade ethyl alcohol and dilute to 1 liter with Type II water.

5.3 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in Type II water. Add 6.4 mL of acetic acid and dilute to 1 liter with Type II water. Make fresh weekly.

5.4 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g EDTA in Type II water and dilute to 1 liter. This solution is also used to clean out the manifold system at end of sampling run.

5.5 Ion exchange resin: Dowex-50 W-X8, ionic form- H^+ . The column is prepared by sucking a slurry of the resin into 12 in. of 3/16-in O.D. tubing. This may be conveniently done by using a pipet and a loose-fitting glass wool plug in the tube. The column, upon exhaustion, turns red. Ensure that air does not enter the column.

5.6 Stock solution: Dissolve 1.4790 g of oven-dried (105°C) Na_2SO_4 in Type II water and dilute to 1 liter in a volumetric flask (1.0 mL = 1.0 mg).

5.7 Standards: Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with Type II water. The following dilutions are suggested.

<u>Stock Solution (mL)</u>	<u>Concentration (mg/L)</u>
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Refrigerate at 4°C .

7.0 PROCEDURE

7.1 Set up manifold as shown in Figure 1. (Note that any precipitated BaSO_4 and the unused barium chloranilate are removed by filtration. If any BaSO_4 should come through the filter, it is complexed by the NaOH-EDTA reagent.)

7.2 Allow both colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place Type II water wash tubes in alternate openings in sampler and set sample timing at 2.0 min.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from Type II water to sampler and begin analysis.

7.6 Calculation:

7.6.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A linear calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A spike duplicate sample is a sample brought through the whole sample preparation and analytical process.

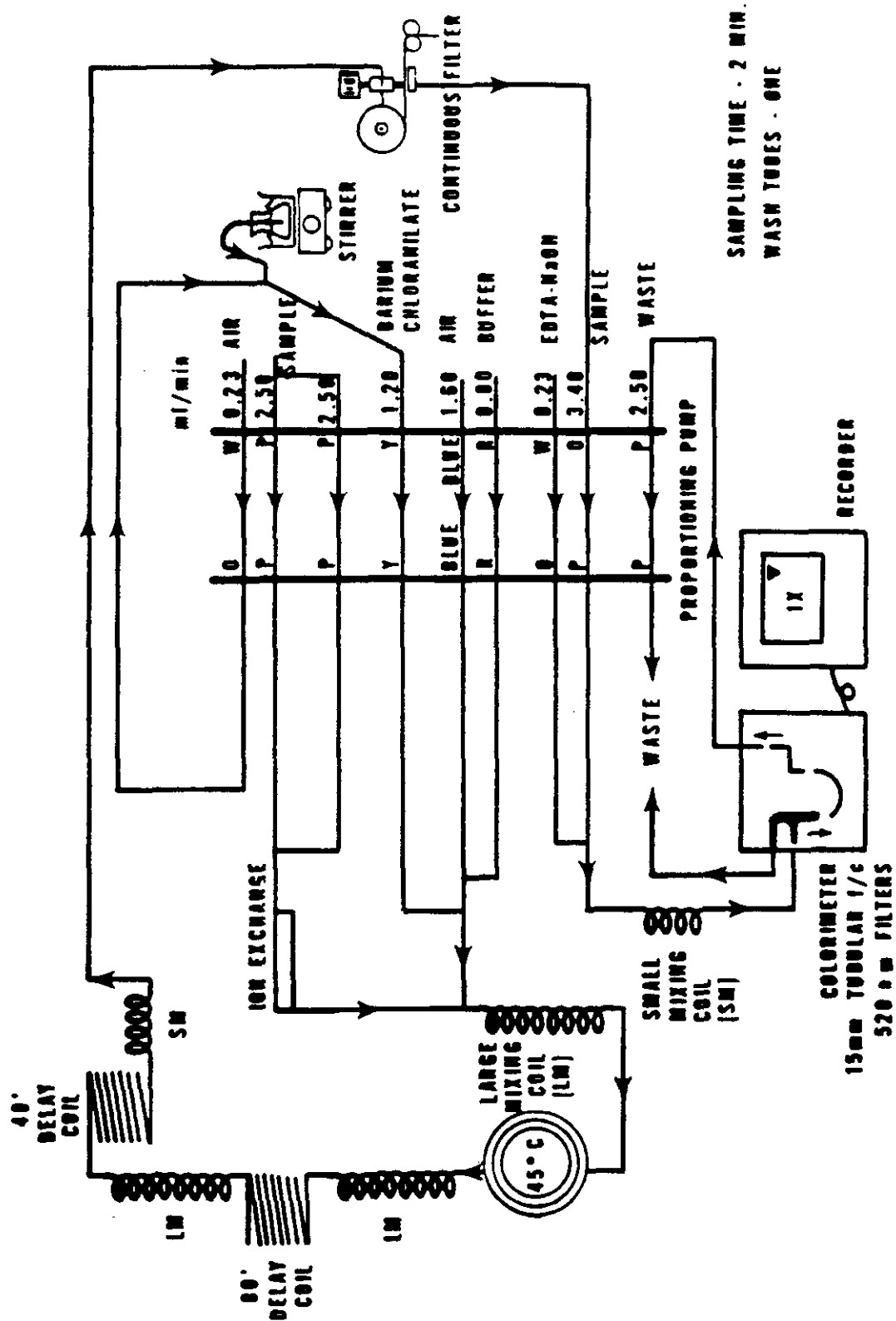


FIGURE 1 - SULFATE MANIFOLD AA-1

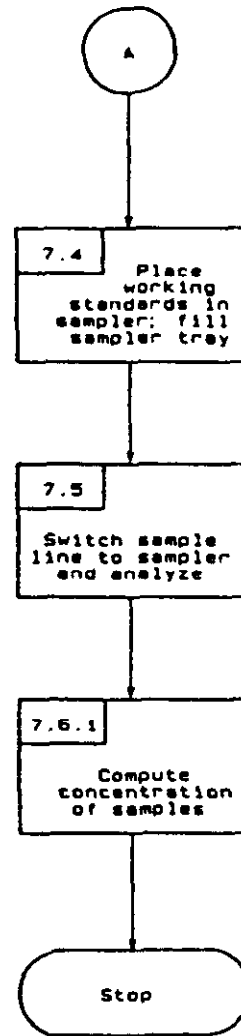
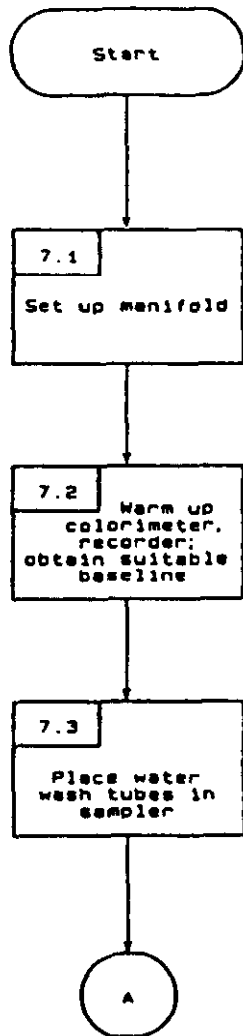
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 375.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Bertolacini, R.J., and J.E. Barney, II, Colorimetric Determination of Sulfate with Barium Chloranilate, Anal. Chem., 29(2), pp. 281-283 (1957).
2. Gales, M.E., Jr., W.H. Kaylor, and J.E. Longbottom, Determination of Sulphate by Automatic Colorimetric Analysis, Analyst, 93, 97 (1968).

METHOD 9035
SULFATE (COLORIMETRIC, AUTOMATED, CHLORANILATE)



METHOD 9040

pH ELECTROMETRIC MEASUREMENT

1.0 SCOPE AND APPLICATION

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

2.0 SUMMARY

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity.

3.2 Sodium error at pH levels >10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with hydrochloric acid (1:9) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 APPARATUS AND MATERIALS

4.1 pH meter: Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer or temperature sensor for automatic compensation.

5.0 REAGENTS

5.1 Primary standard buffer salts are available from the National Bureau of Standards (Special Publication 260) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.2 Secondary standard buffers may be prepared from NBS salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NBS standards and are recommended for routine use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Various instrument designs may involve use of a dial to "balance" or "standardize" or a slope adjustment, as outlined in the manufacturer's instructions. Repeat

adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (<0.1 pH).

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by <0.1 pH units. Two or three volume changes are usually sufficient.

8.0 QUALITY CONTROL

8.1 Duplicate samples and check standards should be analyzed routinely.

8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

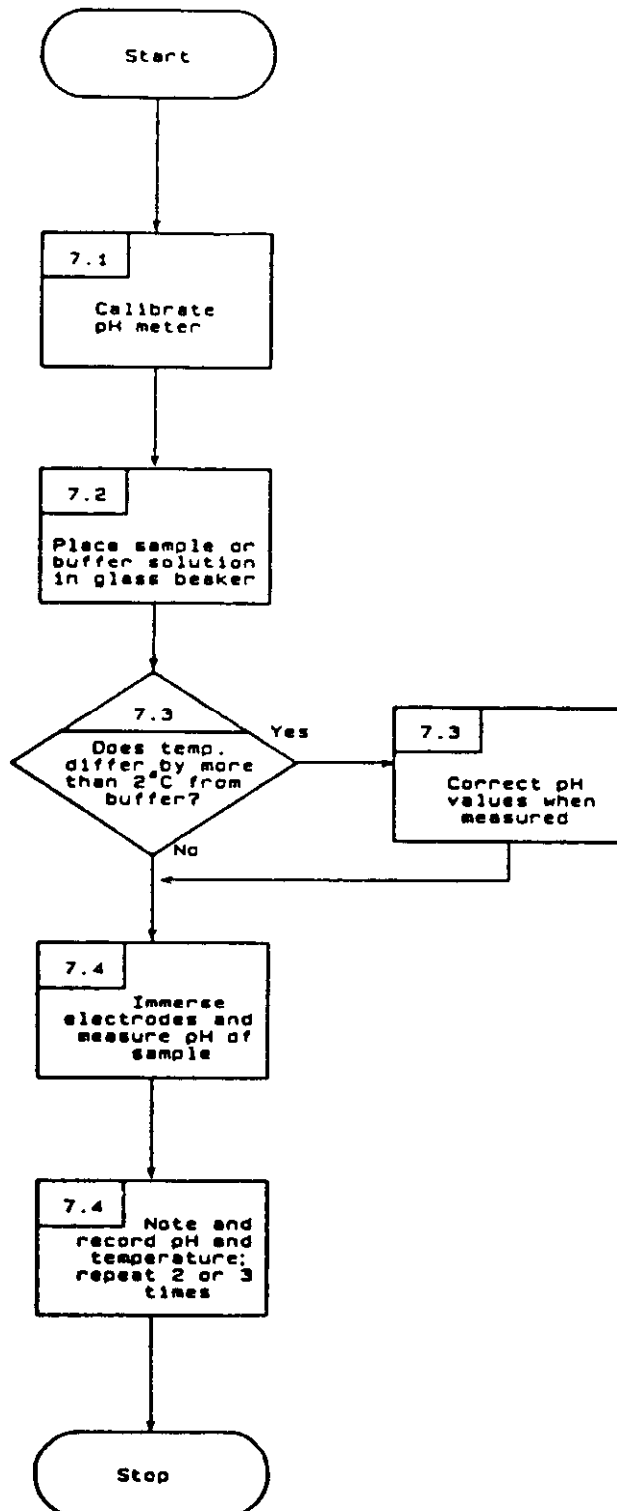
9.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as	
		Bias %	Bias pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

10.0 REFERENCES

1. National Bureau of Standards, Standard Reference Material Catalog 1986-87, Special Publication 260.

METHOD 9040
pH MEASUREMENT



CONDUCTANCE

Method 120.1 (Specific Conductance, μmhos at 25°C)

STORET NO. 00095

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).
2. Summary of Method
 - 2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
 - 2.2 Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.
3. Comments
 - 3.1 Instrument must be standardized with KCl solution before daily use.
 - 3.2 Conductivity cell must be kept clean.
 - 3.3 Field measurements with comparable instruments are reliable.
 - 3.4 Temperature variations and corrections represent the largest source of potential error.
4. Sample Handling and Preservation
 - 4.1 Analyses can be performed either in the field or laboratory.
 - 4.2 If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0.45 micron filter and stored at 4°C. Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use.
5. Apparatus
 - 5.1 Conductivity bridge, range 1 to 1000 μmho per centimeter.
 - 5.2 Conductivity cell, cell constant 1.0 or micro dipping type cell with 1.0 constant. YSI #3403 or equivalent.
 - 5.4 Thermometer
6. Reagents
 - 6.1 Standard potassium chloride solutions, 0.01 M: Dissolve 0.7456 gm of pre-dried (2 hour at 105°C) KCl in distilled water and dilute to 1 liter at 25°C.
7. Cell Calibration
 - 7.1 The analyst should use the standard potassium chloride solution (6.1) and the table below to check the accuracy of the cell constant and conductivity bridge.

Approved for NPDES
Issued 1971.
Editorial revision, 1982

Conductivity 0.01 m KCl

°C	Micromhos/cm
21	1305
22	1332
23	1359
24	1386
25	1413
26	1441
27	1468
28	1496

8. Procedure

- 8.1 Follow the direction of the manufacturer for the operation of the instrument.
- 8.2 Allow samples to come to room temperature (23 to 27°C), if possible.
- 8.3 Determine the temperature of samples within 0.5°C. If the temperature of the samples is not 25°C, make temperature correction in accordance with the instruction in Section 9 to convert reading to 25°.

9. Calculation

- 9.1 These temperature corrections are based on the standard KCl solution.
 - 9.1.1 If the temperature of the sample is below 25°C, add 2% of the reading per degree.
 - 9.1.2 If the temperature is above 25°C, subtract 2% of the reading per degree.
- 9.2 Report results as Specific Conductance, $\mu\text{mhos/cm}$ at 25°.

10. Precision and Accuracy

- 10.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

<u>Increment as</u> <u>Specific Conductance</u>	<u>Precision as</u> <u>Standard Deviation</u>	<u>Bias,</u> <u>%</u>	<u>Accuracy as</u> <u>Bias,</u> <u>$\mu\text{mhos/cm}$</u>
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

- 10.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 $\mu\text{mhos/cm}$ at 25°C, the standard deviation was ± 6 .

Bibliography

1. The procedure to be used for this determination is found in:
Annual Book of ASTM Standards Part 31, "Water," Standard D1125-64, p. 120 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 71, Method 205 (1975).
3. Instruction Manual for YSI Model 31 Conductivity Bridge.
4. Peden, M. E., and Skowron. "Ionic Stability of Precipitation Samples," Atmospheric Environment, Vol. 12, p. 2343-2344, 1978.

ACIDITY

Method 305.1 (Titrimetric)

STORET NO. 70508

1. Scope and Application
 - 1.1 This method is applicable to surface waters, sewages and industrial wastes, particularly mine drainage and receiving streams, and other waters containing ferrous iron or other polyvalent cations in a reduced state.
 - 1.2 The method covers the range from approximately 10 mg/l acidity to approximately 1000 mg/l as CaCO_3 , using a 50 ml sample.
2. Summary of Method
 - 2.1 The pH of the sample is determined and a measured amount of standard acid is added, as needed, to lower the pH to 4 or less. Hydrogen peroxide is added, the solution boiled for several minutes, cooled, and titrated electrometrically with standard alkali to pH 8.2.
3. Definitions
 - 3.1 This method measures the mineral acidity of a sample plus the acidity resulting from oxidation and hydrolysis of polyvalent cations, including salts of iron and aluminum.
4. Interferences
 - 4.1 Suspended matter present in the sample, or precipitates formed during the titration may cause a sluggish electrode response. This may be offset by allowing a 15–20 second pause between additions of titrant or by slow dropwise addition of titrant as the endpoint pH is approached.
5. Apparatus
 - 5.1 pH meter, suitable for electrometric titrations.
6. Reagents
 - 6.1 Hydrogen peroxide (H_2O_2 , 30% solution).
 - 6.2 Standard sodium hydroxide, 0.02 N.
 - 6.3 Standard sulfuric acid, 0.02 N.
7. Procedure
 - 7.1 Pipet 50 ml of the sample into a 250 ml beaker.
 - 7.2 Measure the pH of the sample. If the pH is above 4.0, add standard sulfuric acid (6.3) in 5.0 ml increments to lower the pH to 4.0 or less. If the initial pH of the sample is less than 4.0, the incremental addition of sulfuric acid is not required.
 - 7.3 Add 5 drops of hydrogen peroxide (6.1).
 - 7.4 Heat the sample to boiling and continue boiling for 2 to 4 minutes. In some instances, the concentration of ferrous iron in a sample is such that an additional amount of hydrogen peroxide and a slightly longer boiling time may be required.

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Issued 1971

Technical revision 1974

- 7.5 Cool the sample to room temperature and titrate electrometrically with standard sodium hydroxide (6.2) to pH 8.2.
8. Calculations
- 8.1 Acidity, as mg/1 CaCO_3 =
$$\frac{[(A \times B) - (C \times D)] \times 50,000}{\text{ml of sample}}$$

where:

A = vol. of standard sodium hydroxide used in titration

B = normality of standard sodium hydroxide

C = volume of standard sulfuric acid used to reduce pH to 4 or less

D = normality of standard sulfuric acid

- 8.2 If it is desired to report acidity in millequivalents per liter, the reported values as CaCO_3 are divided by 50, as follows:

$$\text{Acidity as meq/l} = \frac{\text{mg/l } \text{CaCO}_3}{50}$$

9. Precision

- 9.1 On a round robin conducted by ASTM on 4 acid mine waters, including concentrations up to 2000 mg/1, the precision was found to be ± 10 mg/1.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", p 116, D 1067, Method E(1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 277, Method 402(4d) (1975).

CHEMICAL OXYGEN DEMAND

Method 410.4 (Colorimetric, Automated; Manual)

STORET NO. 00340

1. Scope and Application
 - 1.1 This method covers the determination of COD in surface waters, domestic and industrial wastes.
 - 1.2 The applicable range of the automated method is 3–900 mg/l and the range of the manual method is 20 to 900 mg/l.
2. Summary of Method
 - 2.1 Sample, blanks and standards in sealed tubes are heated in an oven or block digester in the presence of dichromate at 150°C. After two hours, the tubes are removed from the oven or digester, cooled and measured spectrophotometrically at 600 nm.
3. Sample Handling and Preservation
 - 3.1 Collect the samples in glass bottles if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
 - 3.2 Samples should be preserved with sulfuric acid to a pH < 2 and maintained at 4°C until analysis.
4. Interferences
 - 4.1 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.
5. Apparatus
 - 5.1 Drying oven or block digester, 150°C
 - 5.2 Corning culture tubes, 16 x 100 mm or 25 x 150 mm with Teflon lined screw cap
 - 5.3 Spectrophotometer or Technicon AutoAnalyzer
 - 5.4 Muffle furnace, 500°C.
6. Reagents
 - 6.1 Digestion solution: Add 10.2 g $K_2Cr_2O_7$, 167 ml conc. H_2SO_4 and 33.3 g $HgSO_4$ to 500 ml of distilled water, cool and dilute to 1 liter.
 - 6.2 Catalyst solution: Add 22 g Ag_2SO_4 to a 4.09kg bottle of conc. H_2SO_4 . Stir until dissolved.
 - 6.3 Sampler wash solution: Add 500 ml of conc H_2SO_4 to 500 ml of distilled water.
 - 6.4 Stock potassium acid phthalate: Dissolve 0.850 g in 800 ml of distilled water and dilute to 1 liter. 1 ml = 1 mg COD
 - 6.4.1 Prepare a series of standard solutions that cover the expected sample concentrations by diluting appropriate volumes of the stock standard.
7. Procedure
 - 7.1 Wash all culture tubes and screw caps with 20% H_2SO_4 before their first use to prevent contamination. Trace contamination may be removed from the tubes by igniting them in a muffle oven at 500°C for 1 hour.

Pending approval for Section 304(h), CWA

Issued 1978

- 7.2. Automated
 - 7.2.1 Add 2.5 ml of sample to the 16 x 100 mm tubes.
 - 7.2.2 Add 1.5 ml of digestion solution (6.1) and mix.
 - 7.2.3 Add 3.5 ml of catalyst solution (6.2) carefully down the side of the culture tube.
 - 7.2.4 Cap tightly and shake to mix layers.
 - 7.2.5 Process standards and blanks exactly as the samples.
 - 7.2.6 Place in oven or block digester at 150°C for two hours.
 - 7.2.7 Cool, and place standards in sampler in order of decreasing concentration. Complete filling sampler tray with unknown samples.
 - 7.2.8 Measure color intensity on AutoAnalyzer at 600 nm.
- 7.3. Manual
 - 7.3.1 The following procedure may be used if a larger sample is desired or a spectrophotometer is used in place of an AutoAnalyzer.
 - 7.3.2 Add 10 ml of sample to 25 x 150 mm culture tube.
 - 7.3.3 Add 6 ml of digestion solution (6.1) and mix.
 - 7.3.4 Add 14 ml of catalyst solution (6.2) down the side of culture tube.
 - 7.3.5 Cap tightly and shake to mix layers.
 - 7.3.6 Place in oven or block digester at 150°C for 2 hours.
 - 7.3.7 Cool, allow any precipitate to settle and measure intensity in spectrophotometer at 600 nm. Use only optically matched culture tubes or a single cell for spectrophotometric measurement.
- 8. Calculation
 - 8.1 Prepare a standard curve by plotting peak height or percent transmittance against known concentrations of standards.
 - 8.2 Compute concentration of samples by comparing sample response to standard curve.
- 9. Precision and Accuracy
 - 9.1 Precision and accuracy data are not available at this time.

Bibliography

- 1. Jirka, A. M., and M. J. Carter, "Micro-Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand." *Anal. Chem.* 47:1397. (1975).

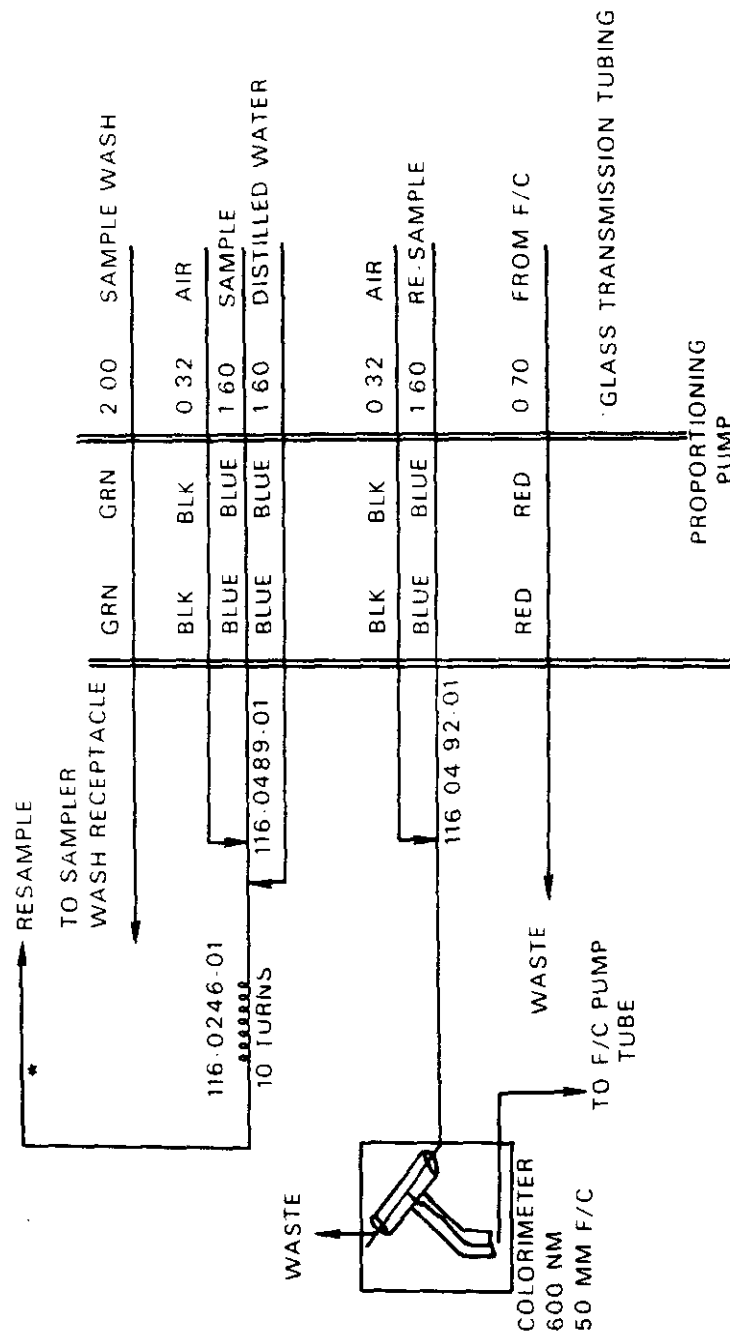


FIGURE 1 C O D MANIFOLD AA1 OR AA 11

METHOD 9060

TOTAL ORGANIC CARBON

1.0 SCOPE AND APPLICATION

1.1 Method 9060 is used to determine the concentration of organic carbon in ground water, surface and saline waters, and domestic and industrial wastes. Some restrictions are noted in Sections 2.0 and 3.0.

1.2 Method 9060 is most applicable to measurement of organic carbon above 1 mg/L.

2.0 SUMMARY OF METHOD

2.1 Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by either catalytic combustion or wet chemical oxidation. The CO_2 formed is then either measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, the manner of preliminary sample treatment as well as the instrument settings will determine which forms of carbon are actually measured. The forms of carbon that can be measured by Method 9060 are:

1. Soluble, nonvolatile organic carbon: e.g., natural sugars.
2. Soluble, volatile organic carbon: e.g., mercaptans, alkanes, low molecular weight alcohols.
3. Insoluble, partially volatile carbon: e.g., low molecular weight oils.
4. Insoluble, particulate carbonaceous materials: e.g., cellulose fibers.
5. Soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter: e.g., oily matter adsorbed on silt particles.

2.3 Carbonate and bicarbonate are inorganic forms of carbon and must be separated from the total organic carbon value. Depending on the instrument manufacturer's instructions, this separation can be accomplished by either a simple mathematical subtraction, or by removing the carbonate and bicarbonate by converting them to CO_2 with degassing prior to analysis.

3.0 INTERFERENCES

3.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter-type syringe or pipet. The openings of the syringe or pipet limit the maximum size of particle which may be included in the sample.

3.3 Removal of carbonate and bicarbonate by acidification and purging with nitrogen, or other inert gas, can result in the loss of volatile organic substances.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

4.2 Apparatus for total and dissolved organic carbon:

4.2.1 Several companies manufacture analyzers for measuring carbonaceous material in liquid samples. The most appropriate system should be selected based on consideration of the types of samples to be analyzed, the expected concentration range, and the forms of carbon to be measured.

4.2.2 No specific analyzer is recommended as superior. If the technique of chemical oxidation is used, the laboratory must be certain that the instrument is capable of achieving good carbon recoveries in samples containing particulates.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities, and should be boiled and cooled to remove CO₂.

5.2 Potassium hydrogen phthalate, stock solution, 1,000 mg/L carbon: Dissolve 0.2128 g of potassium hydrogen phthalate (primary standard grade) in Type II water and dilute to 100.0 mL.

NOTE: Sodium oxalate and acetic acid are not recommended as stock solutions.

5.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with Type II water.

5.4 Carbonate-bicarbonate, stock solution, 1,000 mg/L carbon: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100-mL volumetric flask. Dissolve with Type II water.

5.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to Step 5.3.

NOTE: This standard is not required by some instruments.

5.6 Blank solution: Use the same Type II water as was used to prepare the standard solutions.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE: A brief study performed in the EPA Laboratory indicated that Type II water stored in new, 1-qt cubitainers did not show any increase in organic carbon after 2 weeks' exposure.

6.3 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between sample collection and the start of analysis should be minimized. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

6.4 In instances where analysis cannot be performed within 2 hr from time of sampling, the sample is acidified ($\text{pH} \leq 2$) with HCl or H_2SO_4 .

7.0 PROCEDURE

7.1 Homogenize the sample in a blender.

NOTE: To avoid erroneously high results, inorganic carbon must be accounted for. The preferred method is to measure total carbon and inorganic carbon and to obtain the organic carbon by subtraction. If this is not possible, follow Steps 7.2 and 7.3 prior to analysis; however, volatile organic carbon may be lost.

7.2 Lower the pH of the sample to 2.

7.3 Purge the sample with nitrogen for 10 min.

7.4 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

7.5 For calibration of the instrument, a series of standards should be used that encompasses the expected concentration range of the samples.

7.6 Quadruplicate analysis is required. Report both the average and the range.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Verify calibration with an independently prepared check standard every 15 samples.

8.4 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

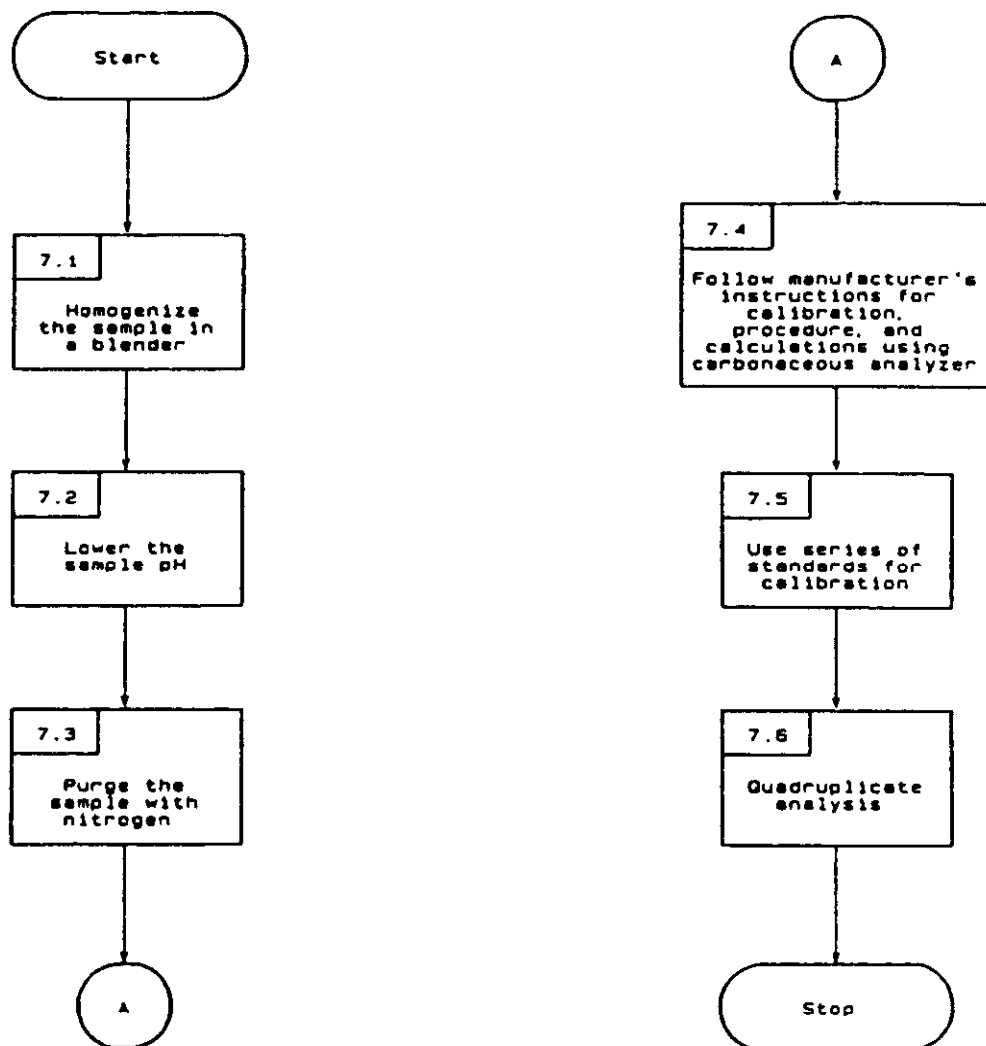
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 415.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 532, Method 505 (1975).

METHOD 9060
TOTAL ORGANIC CARBON



8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for easy reference or inspection.

8.2 All pH determinations must be performed in duplicate.

8.3 Each batch of pH paper must be calibrated versus certified pH buffers or a pH meter which has been calibrated with certified pH buffers.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 8040

PHENOLS

1.0 SCOPE AND APPLICATION

1.1 Method 8040 is used to determine the concentration of various phenolic compounds. Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8040 provides gas chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques (see Chapter Two for guidance). Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 Method 8040 also provides for the preparation of pentafluorobenzyl-bromide (PFB) derivatives, with additional cleanup procedures for electron capture gas chromatography. This is to reduce detection limits of some phenols and to aid the analyst in the elimination of interferences.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required

TABLE 1. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

Compound	Retention time (min)	Method Detection limit (ug/L)
2-sec-Butyl-4,6-dinitrophenol (DNBP)		
4-Chloro-3-methylphenol	7.50	0.36
2-Chlorophenol	1.70	0.31
Cresols (methyl phenols)		
2-Cyclohexyl-4,6-dinitrophenol		
2,4-Dichlorophenol	4.30	0.39
2,6-Dichlorophenol		
2,4-Dimethylphenol	4.03	0.32
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
2-Nitrophenol	2.00	0.45
4-Nitrophenol	24.25	2.8
Pentachlorophenol	12.42	7.4
Phenol	3.01	0.14
Tetrachlorophenols		
Trichlorophenols		
2,4,6-Trichlorophenol	6.05	0.64

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

^aSample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

^bPQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns:

4.1.2.1 Column for underivatized phenols: 1.8-m x 2.0-mm I.D. glass column packed with 1% SP-1240DA on Supelcoport 80/100 mesh or equivalent.

4.1.2.2 Column for derivatized phenols: 1.8-m x 2-mm I.D. glass column packed with 5% OV-17 on Chromosorb W-AW-DMCS 80/100 mesh or equivalent.

4.1.3 Detectors: Flame ionization (FID) and electron capture (ECD).

4.2 Reaction vial: 20-mL, with Teflon-lined cap.

4.3 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.4 Kuderna-Danish (K-D) apparatus:

4.4.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.4.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.4.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

5.0 REAGENTS

5.1 Solvents: Hexane, 2-propanol, and toluene (pesticide quality or equivalent).

5.2 Derivatization reagent: Add 1 mL pentafluorobenzyl bromide and 1 g 18-crown-6-ether to a 50-mL volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly. This operation should be carried out in a hood. Store at 4°C and protect from light.

5.2.1 Pentafluorobenzyl bromide (alpha-Bromopentafluorotoluene): 97% minimum purity.

NOTE: This chemical is a lachrymator.

5.2.2 18-crown-6-ether (1,4,7,10,13,16-Hexaoxacyclooctadecane): 98% minimum purity.

NOTE: This chemical is highly toxic.

5.3 Potassium carbonate: (ACS) Powdered.

5.4 Stock standard solutions:

5.4.1 Prepare stock standard solution at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in 2-propanol and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with 2-propanol. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte as described in Paragraph 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with 2-propanol.

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (if necessary), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with phenolic surrogates (e.g., 2-fluorophenol and 2,4,6-tribromophenol) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of acid surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of less than or equal to 2 with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. Extracts obtained from application of either Method 3540 or 3550 should undergo Acid-Base Partition Cleanup, using Method 3650.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to 2-propanol. The exchange is performed during the micro K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to 95-100°C. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of 2-propanol. A 5-mL syringe is recommended for this operation. Add one or two clean boiling chips to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of 2-propanol to the top. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water.

Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Add an additional 2 mL of 2-propanol, add one or two clean boiling chips to the concentrator tube, and resume concentrating as before. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the extract requires no further derivatization or cleanup, proceed with gas chromatographic analysis.

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column for underivatized phenols: Set nitrogen gas flow at 30 mL/min flow rate. Set column temperature at 80°C and immediately program an 8°C/min temperature rise to 150°C; hold until all compounds have eluted.

7.2.2 Column for derivatized phenols: Set 5% methane/95% argon gas flow at 30 mL/min flow rate. Set column temperature at 200°C isothermal.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used for the underivatized phenols. Refer to Method 8000 for a description of each of these procedures. If derivatization of the phenols is required, the method of external calibration should be used by injecting five or more levels of calibration standards that have also undergone derivatization and cleanup prior to instrument calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.4.2 Phenols are to be determined on a gas chromatograph equipped with a flame ionization detector according to the conditions listed for the 1% SP-1240DA column (Paragraph 7.2.1). Table 1 summarizes estimated

retention times and sensitivities that should be achieved by this method for clean water samples. Practical quantitation limits for other matrices are list in Table 2.

7.4.3 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.4 An example of a GC/FID chromatogram for certain phenols is shown in Figure 1. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

7.4.5 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.6 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.7 If peak detection using the SP-1240DA column with the flame ionization detector is prevented by interferences, PFB derivatives of the phenols should be analyzed on a gas chromatograph equipped with an electron capture detector according to the conditions listed for the 5% OV-17 column (Paragraph 7.2.2). The derivatization and cleanup procedure is outlined in Sections 7.5 through 7.6. Table 3 summarizes estimated retention times for derivatives of some phenols using the conditions of this method.

7.4.8 Figure 2 shows a GC/ECD chromatogram of PFB derivatives of certain phenols.

7.4.9 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.10 Determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. The method of external calibration should be used (see Method 8000 for guidance). The concentration of the individual compounds in the sample is calculated as follows.

$$\text{Concentration (ug/L)} = [(A)(V_t)(B)(D)]/[(V_i)(X)(C)(E)]$$

where:

A = Mass of underivatized phenol represented by area of peak in sample chromatogram, determined from calibration curve (see Method 8000 Paragraph 7.4.2), ng.

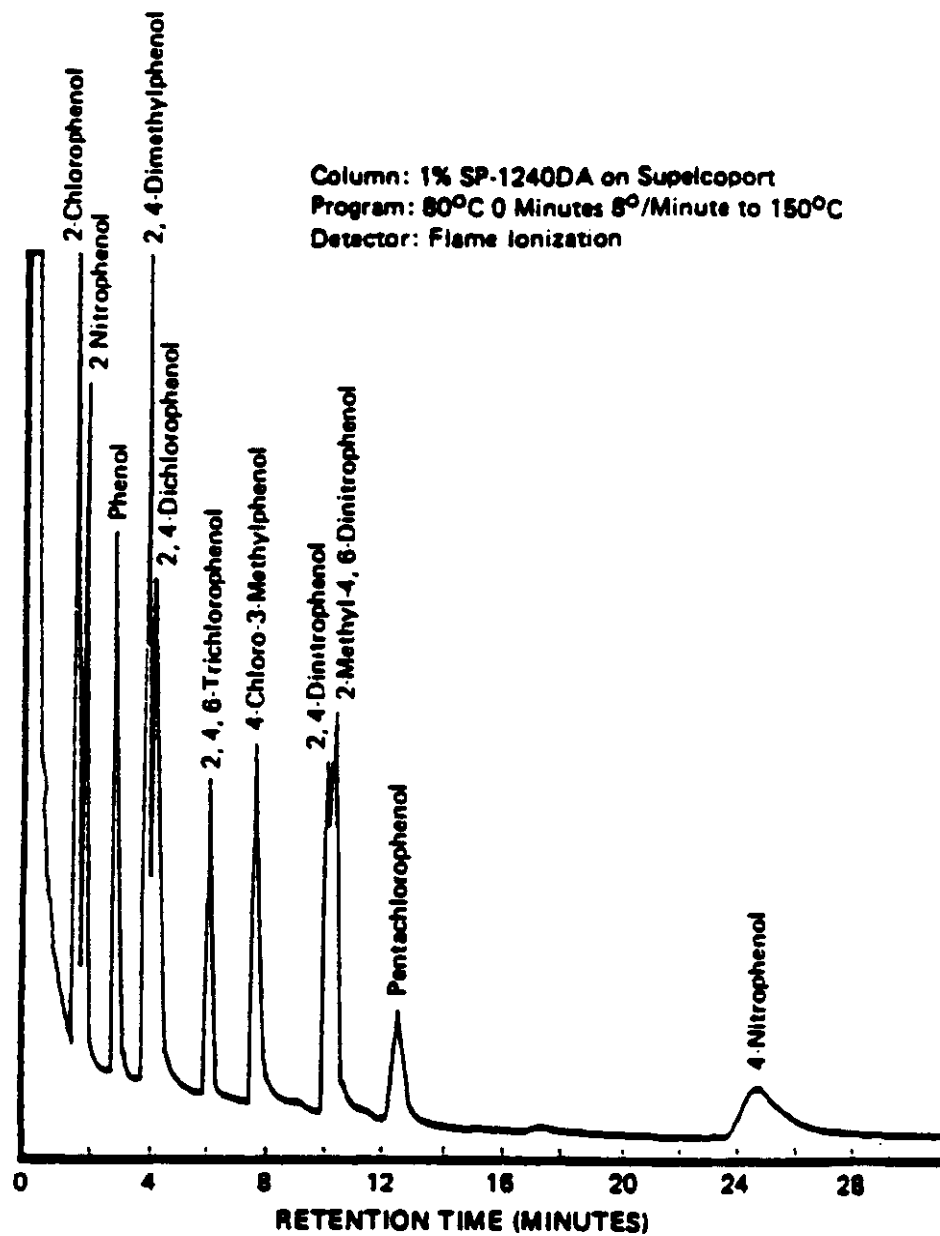


Figure 1. Gas chromatogram of phenols.

TABLE 3. ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFB DERIVATIVES

Parent compound	Retention time (min)	Method detection limit (ug/L)
4-Chloro-2-methylphenol	4.8	1.8
2-Chlorophenol	3.3	0.58
2,4-Dichlorophenol	5.8	0.68
2,4-Dimethylphenol	2.9	0.63
2,4-Dinitrophenol	46.9	
2-Methyl-4,6-dinitrophenol	36.6	
2-Nitrophenol	9.1	0.77
4-Nitrophenol	14.0	0.70
Pentachlorophenol	28.8	0.59
Phenol	1.8	2.2
2,4,6-Trichlorophenol	7.0	0.58

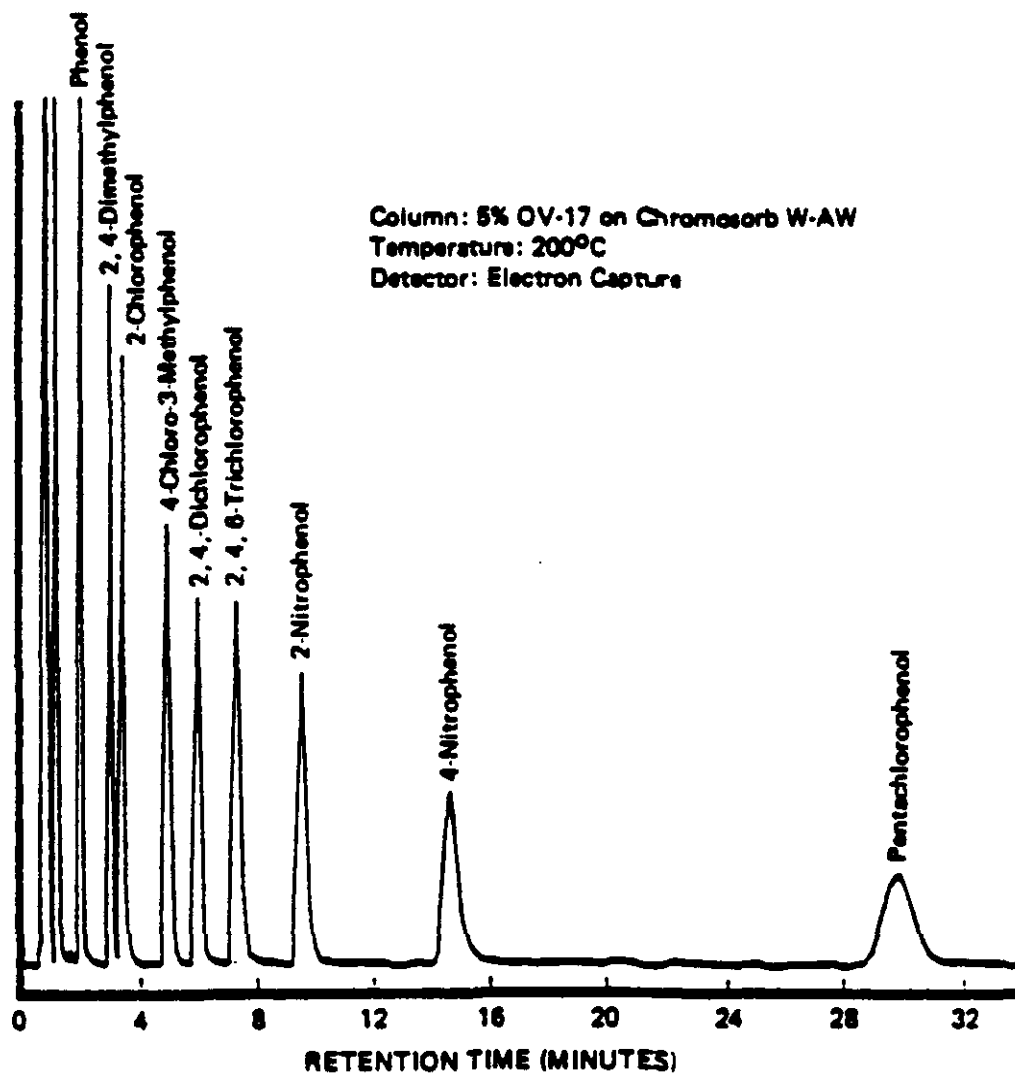


Figure 2. Gas chromatogram of PFB derivatives of phenols.

V_t = Total amount of column eluate or combined fractions from which V_i was taken, μL .

B = Total volume of hexane added in Paragraph 7.5.5, mL.

D = Total volume of 2-propanol extract prior to derivatization, mL.

V_i = Volume injected, μL .

X = Volume of water extracted, mL, or weight of nonaqueous sample extracted, g, from Section 7.1. Either the dry or wet weight of the nonaqueous sample may be used, depending upon the specific application of the data.

C = Volume of hexane sample solution added to cleanup column (Method 3630, Section 7.2), mL.

E = Volume of 2-propanol extract carried through derivatization in Paragraph 7.5.1, mL.

7.5 Derivatization: If interferences prevent measurement of peak area during analysis of the extract by flame ionization gas chromatography, the phenols must be derivatized and analyzed by electron capture gas chromatography.

7.5.1 Pipet a 1.0-mL aliquot of the 2-propanol stock standard solution or of the sample extract into a glass reaction vial. Add 1.0 mL derivatization reagent (Paragraph 5.3). This amount of reagent is sufficient to derivatize a solution whose total phenolic content does not exceed 0.3 mg/mL.

7.5.2 Add approximately 3 mg of potassium carbonate to the solution and shake gently.

7.5.3 Cap the mixture and heat it for 4 hr at 80°C in a hot water bath.

7.5.4 Remove the solution from the hot water bath and allow it to cool.

7.5.5 Add 10 mL hexane to the reaction vial and shake vigorously for 1 min. Add 3.0 mL distilled, deionized water to the reaction vial and shake for 2 min.

7.5.6 Decant the organic layer into a concentrator tube and cap with a glass stopper. Proceed with cleanup procedure.

7.6 Cleanup:

7.6.1 Cleanup of the derivatized extracts takes place using Method 3630 (Silica Gel Cleanup), in which specific instructions for cleanup of the derivatized phenols appear.

7.6.2 Following column cleanup, analyze the samples using GC/ECD, as described starting in Paragraph 7.4.7.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method used. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at a concentration of 100 ug/mL in 2-propanol.

8.2.2 Table 4 indicates the calibration and QC acceptance criteria for this method. Table 5 gives method accuracy and precision as functions of concentration for the analytes. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 12 to 450 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 5.

9.2 The accuracy and precision obtained will be affected by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons and Category 8 - Phenols. Report for EPA Contract 68-03-2625 (in preparation).
2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
3. "Determination of Phenols in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).
4. "EPA Method Validation Study Test Method 604 (Phenols)," Report for EPA Contract 68-03-2625 (in preparation).
5. Kawarabara, F.K. "Microdetermination of Derivatives of Phenols and Mercaptans by Means of Electron Capture Gas Chromatography," Analytical Chemistry, 40, 1009, 1968.
6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.
7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

TABLE 4. QC ACCEPTANCE CRITERIA^a

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for \bar{X} (ug/L)	Range P, P _s (%)
4-Chloro-3-methylphenol	100	16.6	56.7-113.4	99-122
2-Chlorophenol	100	27.0	54.1-110.2	38-126
2,4-Dichlorophenol	100	25.1	59.7-103.3	44-119
2,4-Dimethylphenol	100	33.3	50.4-100.0	24-118
4,6-Dinitro-2-methylphenol	100	25.0	42.4-123.6	30-136
2,4-Dinitrophenol	100	36.0	31.7-125.1	12-145
2-Nitrophenol	100	22.5	56.6-103.8	43-117
4-Nitrophenol	100	19.0	22.7-100.0	13-110
Pentachlorophenol	100	32.4	56.7-113.5	36-134
Phenol	100	14.1	32.4-100.0	23-108
2,4,6-Trichlorophenol	100	16.6	60.8-110.4	53-119

s = Standard deviation of four recovery measurements, in ug/L.

\bar{X} = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

^aCriteria from 40 CFR Part 136 for Method 604. These criteria are based directly upon the method performance data in Table 5. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 5.

TABLE 5. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION^a

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
4-Chloro-3-methylphenol	0.87C-1.97	0.11X-0.21	0.16X+1.41
2-Chlorophenol	0.83C-0.84	0.18X+0.20	0.21X+0.75
2,4-Dichlorophenol	0.81C+0.48	0.17X-0.02	0.18X+0.62
2,4-Dimethylphenol	0.62C-1.64	0.30X-0.89	0.25X+0.48
4,6-Dinitro-2-methylphenol	0.84C-1.01	0.15X+1.25	0.19X+5.85
2,4-Dinitrophenol	0.80C-1.58	0.27X-1.15	0.29X+4.51
2-Nitrophenol	0.81C-0.76	0.15X+0.44	0.14X+3.84
4-Nitrophenol	0.46C+0.18	0.17X+2.43	0.19X+4.79
Pentachlorophenol	0.83C+2.07	0.22X-0.58	0.23X+0.57
Phenol	0.43C+0.11	0.20X-0.88	0.17X+0.77
2,4,6-Trichlorophenol	0.86C-0.40	0.10X+0.53	0.13X+2.40

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of X, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of X, in ug/L.

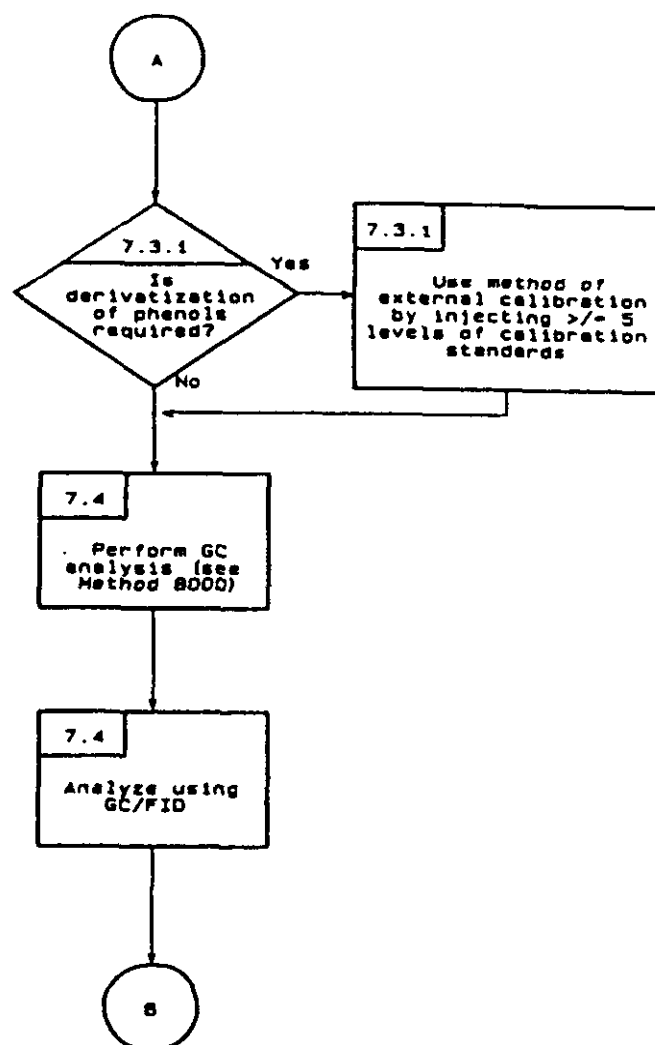
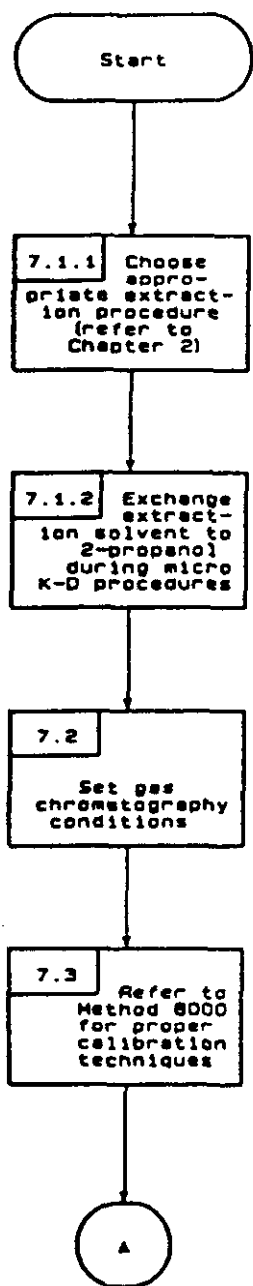
C = True value for the concentration, in ug/L.

X = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

^aFrom 40 CFR Part 136 for Method 604.

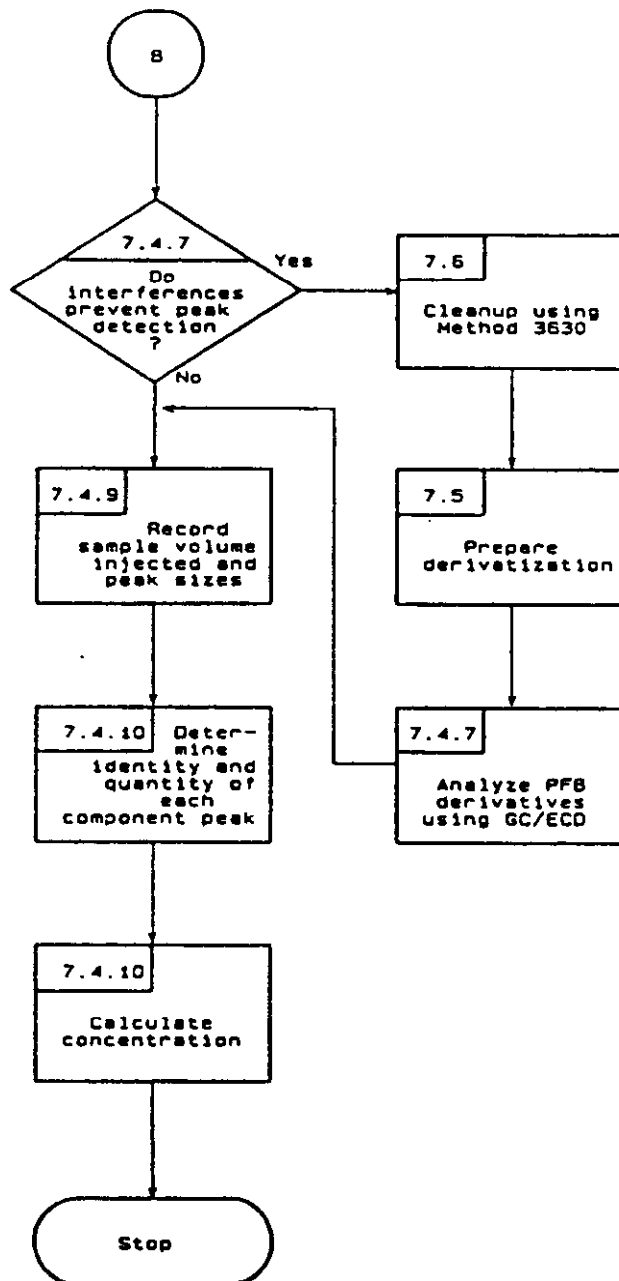
METHOD 8040

PHENOLS



METHOD 8040

PHENOLS
(Continued)



(e) The Administrator will give public notice in the **Federal Register** of the intent to approve or deny a petition and provide an opportunity for public comment. The final decision on a variance from a treatment standard will be published in the **Federal Register**.

(f) A generator, treatment facility, or disposal facility that is managing a waste covered by a variance from the treatment standards must comply with the waste analysis requirements for restricted wastes found under §268.7.

(g) During the petition review process, the applicant is required to comply with all restrictions on land disposal under this part once the effective date for the waste has been reached.

Subpart E—Prohibitions on Stage

[Subpart E added by 51 FR 40636, November 7, 1986]

§268.50 Prohibitions on storage of restricted wastes.

(a) Except as provided in this section, the storage of hazardous wastes restricted from land disposal under Subpart C of this part of RCRA section 3004 is prohibited, unless the following conditions are met:

[268.50(a) introductory paragraph corrected by 52 FR 21014, June 4, 1987; amended by 52 FR 25787, July 8, 1987]

(1) A generator stores such wastes in tanks or containers onsite solely for the purpose of the accumulation of such quantities of hazardous waste as necessary to facilitate proper recovery, treatment, or disposal and the generator complies with the requirements in §262.34 of this chapter. (A generator who is in existence on the effective date of a regulation under this part and who must store hazardous wastes for longer than 90 days due to the regulations under this Part becomes an owner/operator of a storage facility and must obtain a RCRA permit. Such a facility may qualify for interim status upon compliance with the regulations governing interim status under 40 CFR 270.70).

[268.50(a)(1) corrected by 52 FR 21014, June 4, 1987]

(2) An owner/operator of a hazardous waste treatment, storage, or disposal facility stores such wastes in tanks or containers solely for the purpose of the accumulation of such quantities of hazardous waste as necessary to facilitate proper recovery, treatment, or disposal and:

(i) Each container is clearly marked to identify its contents and the date each period of accumulation begins;

(ii) Each tank is clearly marked with a description of its contents, the quantity of each hazardous waste received, and the date each period of accumulation begins, or such information for each tank is recorded and maintained in the operating record at that facility. Regardless of whether the tank itself is marked, an owner/operator must comply with the operating record requirements specified in § 264.73 or § 265.73.

[268.50(a)(2) revised by 52 FR 21014, June 4, 1987]

(3) A transporter stores manifested shipments of such wastes at a transfer facility for 10 days or less.

[268.50 (a)(3) corrected by 52 FR 21014, June 4, 1987]

(b) An owner/operator of a treatment, storage or disposal facility may store such wastes for up to one year unless the Agency can demonstrate that such storage was not solely for the purpose of accumulation of such quantities of hazardous waste as are necessary to facilitate proper recovery, treatment, or disposal.

(c) An owner/operator of a treatment, storage or disposal facility may store such wastes beyond one year; however, the owner/operator bears the burden of proving that such storage was solely for the purpose of accumulation of such quantities of hazardous waste as are necessary to facilitate proper recovery, treatment, or disposal.

(d) The prohibition in paragraph (a) of this section does not apply to the wastes which are the subject of an approved petition under §268.6 or a nationwide variance contained in Subpart C of this part or an approved case-by-case extension under §268.5

[268.50(d) corrected by 52 FR 21014, June 4, 1987]

[268.50(e) revised and (f) added by 52 FR 25787, July 8, 1987]

(e) The prohibition in paragraph (a) of this section does not apply to hazardous wastes that meet the treatment standards specified under §§ 268.41, 268.42, and 268.43 or the treatment standards specified under the variance in § 268.44, or, where treatment standards have not been specified, is in compliance with the applicable prohibitions specified in § 268.32 or RCRA section 3004.

(f) Liquid hazardous wastes containing polychlorinated biphenyls (PCBs) at concentrations greater than or equal to 50 ppm must be stored at a facility that meets the requirements of 40 CFR 761.65(b) and must be removed from storage and treated or disposed as required by this part within one year of the date when such wastes are first placed into storage. The provisions of paragraph (c) of this section do not apply to such PCB wastes prohibited under § 268.32 of this part

Appendix I to Part 268 — Toxicity Characteristic Leaching Procedure (TCLP)

[Appendix I added by 51 FR 40636, November 7, 1986]

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual contaminants are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

2.0 SUMMARY OF METHOD (see Figure 1)

2.1 For liquid wastes (i.e., those containing insignificant solid material), the waste, after filtration through a 0.6- to 0.8-um glass fiber filter, is defined as the TCLP extract.

2.2 For wastes comprised of solids or for wastes containing significant amounts of solid material, the particle-size of the waste is reduced (if necessary), the liquid phase, if any, is separated from the solid phase and stored for later analysis. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction

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fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatiles (See Table 1). Following extraction, the liquid extract is separated from the solid phase by 0.6- to 0.8- μ m glass fiber filter filtration.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 *Agitation apparatus:* An acceptable agitation apparatus is one which is capable of rotating the extraction vessel in an end-over-end fashion (See Figure 2) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessel:

4.2.1 *Zero-Headspace Extraction Vessel (ZHE):* This device is for use only when the waste is being tested for the mobility of volatile constituents (see Table 1). The ZHE is an extraction vessel that allows for liquid/solid separation within the device, and which effectively precludes headspace (as depicted in Figure 3). This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without having to open the vessel (see Step 4.3.1). These vessels shall have an internal volume of 500 to 600 ml. and be equipped to accommodate a 90-mm filter. Suitable ZHE devices known to EPA are identified in Table 3. These devices contain viton O-rings which should be replaced frequently.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analysis and the manufacturer should be contacted.

The ZHE should be checked after every extraction. If the device contains a built-in

pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

4.2.2 When the waste is being evaluated for other than volatile contaminants, an extraction vessel that does not preclude headspace (e.g., a 2-liter bottle) is used. Suitable extraction vessels include bottles made from various materials, depending on the contaminants to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used over other types of glass, especially when inorganics are of concern. Plastic bottles may be used only if inorganics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.2.3 Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 9.0) refers to pounds-per-square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.3 *Filtration Devices:* It is recommended that all filtrations be performed in a hood.

4.3.1 *Zero-Headspace Extractor Vessel* (see Figure 3): When the waste is being evaluated for volatiles, the zero-headspace extraction vessel is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

Note. — When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 *Filter Holder:* When the waste is being evaluated for other than volatile compounds, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation is used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (Filter holders having an internal capacity of 1.5L or greater and equipped to accommodate at 142 mm diameter filter are recommended). Vacuum filtration is only recommended for wastes with low solids content (<10%) and for highly granular (liquid-containing) wastes. All other types of wastes should be filtered using positive pressure filtration. Filter holders known to EPA to be suitable for use are shown in Table 4.

4.3.3 Materials of Construction:

Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE) polypropylene, or polyvinyl chloride may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics and constituents of concern.

4.4 *Filters:* Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6- to 0.8- μ m, or equivalent. Filters known to EPA to meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1.0 N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 *pH meters:* Any of the commonly available pH meters are acceptable.

4.6 *ZHE extract collection devices:* TEDLAR® bags or glass, stainless steel or

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PTFE gas tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions.

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of non-aqueous liquid (i.e., <1% of total waste), the TEDLAR® bag should be used to collect and combine the initial liquid and solid extract. The syringe is not recommended in these cases.

4.6.2 If a waste contains a significant amount of non-aqueous initial liquid phase (i.e., > 1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 *ZHE extraction fluid transfer devices*: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a constant displacement pump, a gas tight syringe, pressure filtration until (See Step 4.3.2), or another ZHE device).

4.8 *Laboratory balance*: Any laboratory balance accurate to within ± 0.01 grains may be used (all weight measurements are to be within ± 0.1 grams).

5.0 REAGENTS

5.1. *Reagent water*: Reagent water is defined as water in which an interference is not observed at or above the method detection limit of the analyte(s) of interest. For non-volatile extractions, ASTM Type II water, or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.1.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.1.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at $90 \pm 5^\circ\text{C}$, bubble a contaminant-free inert gas (e.g., nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.2 1.0 N Hydrochloric acid (HCl) made from ACS reagent grade.

5.3 1.0 N Nitric acid (HNO₃) made from ACS reagent grade.

5.4 1.0 N Sodium hydroxide (NaOH) made from ACS reagent grade.

5.5 Glacial acetic acid (HOAc) ACS reagent grade.

5.6 Extraction fluid:

5.6.1 Extraction fluid #1: This fluid is made by adding 5.7 mL glacial HOAc to 500 mL of the appropriate water (see Step 5.1), adding 64.3 mL of 1.0 N NaOH, and diluting to a volume of 1 liter. When correctly prepared the pH of this fluid will be 4.93 ± 0.05 .

5.6.2 Extraction fluid #2: This fluid is made by diluting 5. mL glacial HOAc with ASTM Type II water (see Step 5.1) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05 .

Note. — It is suggested that these extraction fluid be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately.

5.7 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 At least two separate representative samples of a waste should be collected. If volatile organics are of concern, a third sample should be collected. The first sample is used in several preliminary TCLP evaluations (e.g., to determine the percent solids of the waste; to determine if the waste contains insignificant solids (i.e., the waste is its own extract after filtration); to determine if the solid portion of the waste

requires particle-size reduction; and to determine which of the two extraction fluids are to be used for the non-volatile TCLP extraction of the waste). These preliminary evaluations are identified in Section 7.0. The second and, if required, third samples are extracted using the TCLP non-volatile procedure (Section 8.0) and volatile procedure (Section 9.0), respectively.

6.3 Preservatives shall not be added to samples.

6.4 Samples can be refrigerated unless refrigeration results in irreversible physical change to the waste (e.g., precipitation).

6.5 When the waste is to be evaluated for volatile contaminants care should be taken to minimize the loss of volatiles. Samples shall be taken and stored in a manner to prevent the loss of volatile contaminants. If possible, it is recommended that any necessary particle-size reduction should be conducted as the sample is being taken (See Step 8.5).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. If they need to be stored, even for a short period of time, storage shall be at 4°C , and samples for volatiles analysis shall not be allowed to come into contact with the atmosphere (i.e., no headspace). See Section 10.0 (QA requirements) for acceptable sample and extract holding times.

7.0 PRELIMINARY TCLP EVALUATIONS

The preliminary TCLP evaluations are performed on a minimum 100 gram representative sample of waste that will not actually undergo TCLP extraction (designated as the first sample in Step 6.2). These evaluations include preliminary determination of the percent solids of the waste; determination of whether the waste contains insignificant solids, and is therefore its own extract after filtration; determination of whether the solid portion of the waste requires particle-size reduction; and determination of which of the two extraction fluids are to be used for the non-volatile TCLP extraction of the waste.

7.1 *Preliminary determination of percent solids*: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

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7.1.1 If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Step 7.4.

7.1.2 If the sample is liquid or multiphase, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.1.3 through 7.1.9.

7.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.5 Weigh out a representative subsample of the waste (100 gram minimum) and record the weight.

7.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). If filtration of the waste at 4°C reduces the amount of expressed liquid over that would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

Note.—If waste material (>1% of original sample weight) gas obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressuring gas

moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10-psi, if the pressuring gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2-minute period), filtration is stopped.

Note.—Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note.—Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. But even after applying vacuum or pressure filtration, as outlined in Step 7.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. The original filter is *not* to be replaced with a fresh filter under any circumstances. Only one filter is used.

7.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (See Step 7.1.3) from the total weight of the filtrate-filled container. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Step 7.1.5 or 7.1.7. Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.9)}}{\text{Total weight of waste (Step 7.1.5 or 7.1.7)}} \times 100$$

7.2 Determination of whether waste is liquid or has insignificant amounts of solid material: If the sample obviously has a significant amount of solid material, the solid phase must be subjected to extraction; proceed to Step 7.3 to determine if the waste requires particle-size reduction (and to reduce particle-size, if necessary).

Determine whether the waste is liquid or has insignificant amounts of solid material (which need not undergo extraction) as follows:

7.2.1 Remove the solid phase and filter from the filtration apparatus.

7.2.2 Dry the filter and solid phase at $100 \pm 20^\circ\text{C}$ until two successive weighings

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yield the same value within $\pm 1\%$. Record final weight.

Note.—Caution should be taken to insure that the subject solid will not flash

upon heating. It is recommended that the drying oven be vented to a hood or appropriate device.

7.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{Weight of dry waste and filter} - \text{tared weight of filter}}{\text{Initial weight of waste (Step 7.1.5 or 7.1.1)}} \times 100$$

[7.2.3 equation corrected by 52 FR 21014, June 4, 1987]

7.2.4 If the percent dry solids is less than 0.5%, consult Step 6.2 and proceed to Section 8.0 if non-volatiles in the waste are of concern, and to Section 9.0 if volatiles are of interest. In this case, the waste, after filtration is defined as the TCLP extract. If the percent dry solids is greater than or equal to 0.5%, and if the non-volatile TCLP is to be performed, return to the beginning of this Section (7.0) with a new representative waste sample, so that it can be determined if particle-size reduction is necessary (Step 7.3), and so that the appropriate extraction fluid may be determined (Step 7.4) on a fresh portion of the solid phase of the waste. If only the volatile TCLP is to be performed, see the Note in Step 7.4.

7.3 *Determination of whether the wastes requires particle-size reduction (particle-size is reduced during this Step):* Using the solid portion of the waste, evaluate the solid for particle-size. If the solid has a surface area per gram of material equal to or greater than 3.1 cm², or is smaller than 1 cm in its narrowest dimension (e.g., is capable of passing through a 9.5-mm (0.375-inch) standard sieve), particle-size reduction is not required (proceed to Step 7.4). If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described above.

Note.—Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not required; nor is it recommended.

7.4 *Determination of appropriate extraction fluid:* If the solid content is great-

er than or equal to 0.5% of the waste and if TCLP extraction for non-volatile constituents will take place (Section 8.0), determination of the appropriate fluid (Step 5.6) to use for the non-volatiles extraction is performed as follows.

Note.—TCLP extraction for volatile constituents entails using only extraction fluid #1 (Step 5.6.1). Therefore, if TCLP extraction for non-volatiles extraction is not required, proceed to section 9.0.

7.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle-size of approximately 1mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500-mL beaker or Erlenmeyer flask.

[7.4.1 corrected by 50 FR 21014, June 4, 1987]

7.4.2 Add 96.5 mL of reagent water (ASTM Type II) to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is ≤ 5.0 , extraction fluid #1 is used. Proceed to Section 8.0.

7.4.3 If the pH from Step 7.4.2 is > 5.0 , add 3.5 mL 1.0 N HCl, slurry briefly, cover with a watchglass, heat to 50° C, and hold at 50° C for 10 minutes.

7.4.4 Let the solution cool to room temperature and record the pH. If the pH is ≤ 5.0 , use extraction fluid #1. If the pH is > 5.0 , use extraction fluid #2. Proceed to Section 8.0.

7.5 The sample of waste used for performance of this Section shall *not* be used any further. Other samples of the waste (see Step 6.2) should be employed for the Section 8.0 and 9.0 extractions.

8.0 PROCEDURE WHEN VOLATILES ARE NOT INVOLVED

Although a minimum sample size of 100 grams (solid and liquid phases) is required, a larger sample size may be more appropriate, depending on the solids content of the waste sample (percent solids, see Step 7.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by the performance of a single TCLP extraction will not be sufficient to perform all of the analyses to be conducted, it is recommended that more than one extraction be performed and that the extracts from each extraction be combined and then aliquoted for analysis.

8.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Step 7.1), weigh out a representative subsample of the waste (100 grams minimum) and proceed to Step 8.9.

8.2 If the sample is liquid or multiphase, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 8.3 to 8.8.

8.3 Pre-weigh the container that will receive the filtrate.

8.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (See Step 4.4).

Note.—Acid washed filters may be used for all non-volatile extractions even when metals are not of concern.

8.5 Weigh out a representative subsample of waste (100 grams minimum) and record the weight. If the waste was shown to contain $< 0.5\%$ dry solids (Step 7.2), the waste, after filtration is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing $\geq 0.5\%$ dry solids (Steps 7.1 or 7.2), use the percent solids information obtained in Step 7.1 to determine the optimum sample size (100

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gram minimum) for filtration. Enough solids should be generated after filtration to support the analyses to be performed on the TCLP extract.

[8.5 corrected by 52 FR 21014, June 4, 1987]

8.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

8.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Step 4.3.2). If filtration of the waste at 4° C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Note. — If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 8.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1–10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10-psi increments to maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), filtration is stopped.

Note. — Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

8.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Step 8.13) or stored at 4° C until time of analysis.

Note. — Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. But even after applying vacuum or pressure filtration, as outlined in Step 8.7, this material may not filter. If this is the case, the material within the filtration devices defined as a solid and is carried through the extraction as a solid. The original filter is *not* to be replaced with a fresh filter under any circumstances. Only one the filter is used.

[8.8 note corrected by 52 FR 21014, June 4, 1987]

8.9 If the waste contains <0.5% dry solids (see Step 7.2), proceed to Step 8.13. If the waste contains ≤0.5% dry solids (see Step 7.1 or 7.2), and if particle-size reduction of the solid was needed in Step 7.3, proceed to Step 8.10. If particle-size reduction was not required in Step 7.3, quantitatively transfer the solid material into the extractor vessel, including the

filter used to separate the initial liquid from the solid phase. Proceed to Step 8.11.

8.10 The solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to a surface area of particle-size as described in Step 7.3. When the surface area of particle-size has been appropriately altered, quantitatively transfer the solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase.

Note. — Sieving of the waste through a sieve that is not Teflon coated should not be done due to avoid possible contamination of the sample. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

8.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \% \text{ solids (Step 7.1)} = \text{weight of waste filtered (Step 8.5 or 8.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction is to take place) shall be maintained at $22 \pm 3^\circ \text{C}$ during the extraction period.

Note. — As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

8.12 Following the 18 ± 2 hour extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 8.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if

necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

8.13 The TCLP extract is now prepared as follows:

8.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 8.12 is defined as the TCLP extract. Proceed to Step 8.14.

8.13.2 If compatible (e.g., multiple phases will not result on combination), the filtered liquid resulting from Step 8.12 is combined with the initial liquid phase of the waste as obtained in Step 8.7. This combined liquid is defined as the TCLP extract. Proceed to Step 8.14.

8.13.3 If the initial liquid phase of the waste, as obtained from Step 8.7, is not or may not be compatible with the filtered liquid resulting from Step 8.12, these liquids are not combined. These liquids, collectively defined as the TCLP extract, are analyzed separately, and the results are combined mathematically. Proceed to Step 8.14.

8.14 Following collection of the TCLP extract, it is recommended that the pH of the extract be recorded. The extract

should be immediately aliquoted for analysis and properly preserved (metals aliquots must be acidified with nitric acid to pH ≤ 2 ; all other aliquots must be stored under refrigeration (4°C) until analyzed). The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals, other than mercury, shall be acid digested. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm 0.5\%$), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).

C_1 = The concentration of the contaminant of concern in the first phase (mg/L).

V_2 = The volume of the second phase (L).

C_2 = The concentration of the contaminant of concern in the second phase (mg/L).

8.15 The contaminant concentrations in the TCLP extract are compared with the thresholds identified in the appropriate regulations. Refer to Section 10.0 for quality assurance requirements.

9.0 PROCEDURE WHEN VOLATILES ARE INVOLVED

The ZHE device is used to obtain TCLP extracts for volatile analysis only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500-mL internal capacity. Although a minimum sample size of 100 grams was required in the Section 8.0 procedure, the ZHE can only accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no liquid (additional) may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

The ZHE is charged with sample only once and the device is not opened until the final extract (of the solid) has been collected. Repeated filling of the ZHE of

obtain 25 grams of solid is not permitted. The initial filtrate should be weighed and then stored at 4 °C until either analyzed or recombined with the final extract of the solid.

Although the following procedure allows for particle-size reduction during the conduct of the procedure, this could result in the loss of volatile compounds. If possible (e.g., particle-size may be reduced easily by crumbling), particle-size reduction (See Step 9.2) should be conducted on the sample as it is being taken. If necessary, particle-size reduction may be conducted during the procedure.

In carrying out the following steps, do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

9.1 Pre-weigh the (evacuated) container which will receive the filtrate (See Step 4.6), and set aside. If using a TEDLAR® bag, all liquid must be expressed from the device, whether it be for the initial or final liquid/solid separation, and an aliquot taken from the liquid in the bag, for analysis. The containers listed in Step 4.6 are recommended for use under the following conditions.

9.1.1 If a waste contains an aqueous liquid phase or if the waste does not contain a significant amount of non-aqueous liquid (i.e., $< 1\%$ of total waste), the TEDLAR® bag should be used to collect and combine the initial liquid and solid extract. The syringe is not recommended in these cases.

9.1.2. If a waste contains a significant amount of non-aqueous initial liquid phase (i.e., $> 1\%$ of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

9.1.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL liquid expressed from the device. The remaining aliquots are used for analysis.

9.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within

the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 9.0, Step 7.1 and/or 7.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

[9.2 corrected by 52 FR 21014, June 4, 1987]

9.3 If the waste is 100% solid (see Step 7.1) weigh out a representative subsample (25 gram maximum) of the waste, record weight, and proceed to Step 9.5.

9.4 If the waste was shown to contain $< 0.5\%$ dry solids (Step 7.2), the waste, after filtration is defined as the TCLP extract. Enough of the sample should be filtered so that the amount of filtered liquid will support all of the volatile analyses required. For wastes contains $\leq 0.5\%$ dry solids (Steps 7.1 and/or 7.2), use the percent solids information obtained in Step 7.1 to determine the optimum sample size to charge into the ZHE. The appropriate sample size recommended is as follows:

9.4.1 For wastes containing $\leq 5\%$ solids (see Step 7.1), weigh out a representative 500 gram sample or waste and record the weight.

9.4.2 For wastes containing $> 5\%$ solids (see Step 7.1), the amount of waste to charge into the ZHE is determined as follows:

$$\text{Weight of waste to charge} = \frac{\text{ZHE}}{\% \text{ solids (Step 7.1)}} \times 100$$

Weigh out a representative subsample of the waste of the appropriate size and record the weight.

9.5 If particle-size reduction of the solid portion of the waste was required in Step 7.3, proceed to Step 9.6. If particle-size reduction was not required in Step 7.3, proceed to Step 9.7.

9.6. The waste is prepared for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle-size as described in Step 7.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction

[Appendix I]

tion must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

Note. — Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 9.7.

9.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Wastes that settle slowly shall not be centrifuged prior to filtration.

9.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). *Do not* attach the extraction collection device to the top plate.

Note. — If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 9.4, to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1–10 psi (or more if necessary) to force all headspace (into a hood) slowly out of the ZHE device. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Step 7.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Step 9.12.

9.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1–10 psi to force the liquid phase into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within any 2-minute period, filtration is stopped. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect the filtrate collection container.

Note. — Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

9.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

Note. — Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. But even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Step 7.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Step 9.15.

9.11 The liquid phase may now be either analyzed immediately (see Steps 9.13 through 9.15) or stored at 4°C under minimal headspace conditions until time of analysis. The weight of extraction fluid #1 to add to the ZHE is determined as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \% \text{ solids (Step 7.1)} \times \text{weight of waste filtered (Step 9.4 or 9.8)}}{100}$$

[9.11 equation corrected by 52 FR 21014, June 4, 1987]

9.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Step 5.6).

9.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

9.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Physically rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Put 5–10 psi behind the piston (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5–10 psi and check all ZHE fittings to ensure that they are closed.

9.12.3 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate the ZHE at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction is to occur) shall be maintained at $22 \pm 3^\circ\text{C}$ during agitation.

9.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and redo the extraction with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste, unless doing so

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would create multiple phases, or unless there is not enough volume left within the filtrate collection container. A separate filtrate collection container must be used in these cases. Filter through the glass fiber filter, using the ZHE device as discussed in Step 9.9. All extract shall be filtered and collected in the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 9.1).

Note. — An in-line glass fiber filter may be used to filter the material within the ZHE when it is suspected that the glass fiber filter has been ruptured.

9.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Step 9.13 is defined as the TCLP extract. If the waste contained in initial liquid phase, the filtered liquid material obtained from Step 9.13 and the initial liquid phase (Step 9.9) are collectively defined as the TCLP extract.

9.15 Following collection of the TCLP extract, the extract should be immediately aliquoted for analysis and stored with minimal headspace at 4°C until analyzed. The TCLP extract will be prepared and analyzed according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to $\pm 0.5\%$), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
 C_1 = The concentration of the contaminant of concern in the first phase (mg/L).

V_2 = The volume of the second phase (L).

C_2 = The concentration of the contaminant of concern in the second phase (mg/L).

9.16 The contaminant concentrations in the TCLP extract are compared with the thresholds identified in the appropriate regulations. Refer to Section 10.0 for quality assurance requirements.

10.0 QUALITY ASSURANCE REQUIREMENTS

10.1 All data, including quality assurance data, should be maintained and available for reference or inspection.

10.2 A minimum of one blank (extraction fluid #1) for every 10 extractions that have been conducted in an extraction vessel shall be employed as a check to determine if any memory effects from the extraction equipment are occurring.

10.3 For each analytical batch (up to twenty samples), it is recommended that a matrix spike be performed. Addition of matrix spikes should occur once the TCLP extract has been generated (i.e., should not occur prior to performance of the TCLP procedure). The purpose of the matrix spike is to monitor the adequacy of the analytical methods used on the TCLP extract and for determining if matrix interferences exist in analyte detection.

10.4 All quality control measures described in the appropriate analytical methods shall be followed.

10.5 The method of standard addition shall be employed for each analyte if: 1) recovery of the compound from the TCLP extract is not between 50 and 150%, or 2) if

the concentration of the constituent measured in the extract is within 20% of the appropriate regulatory threshold. If more than one extraction is being run on samples of the same waste (up to twenty samples), the method of standard addition need be applied only once and the percent recoveries applied to the remainder of the extractions.

10.6 Samples must undergo TCLP extraction within the following time period after sample receipt: Volatiles, 14 days; Semi-Volatiles, 40 days; Mercury, 28 days; and other Metals, 180 days. Extraction of the solid portion of the waste should be initiated as soon as possible following initial solid/liquid separation. TCLP extracts shall be analyzed after generation and preservation within the following periods: Volatiles, 14 days; Semi-Volatiles, 40 days; Mercury, 28 days; and other Metals, 180 days.

TABLE 1.—VOLATILE CONTAMINANTS¹

Compound	CAS No.
Acetone	67-64-1
n-Butyl alcohol	71-36-6
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	109-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
Xylene	1330-20-7

¹ Includes compounds identified in the Land Disposal Restrictions Rule. If any or all of these compounds are of concern, the zero-headspace extractor vessel shall be used. If other (non-volatile) compounds are of concern, the conventional bottle extractor shall be used.

TABLE 2.—SUITABLE ROTARY AGITATION APPARATUS¹

Company	Location	Model
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5899	4-vessel device, 6-vessel device
Lars Landa Manufacturing	Whitmore Lake, MI (313) 449-4116	10 vessel device, 5 vessel device
IRA Machine Shop and Laboratory	Sanitice, PR (809) 752-4004	15-vessel device
EPRI Extractor		6-vessel device ²
REXNORD	Milwaukee, WI (414) 543-2850	6-vessel device

TABLE 2.—SUITABLE ROTARY AGITATION APPARATUS¹—Continued

Company	Location	Model
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel device

¹ Any device that rotates the extraction vessel in an end-over-end fashion at 30 \pm 2 rpm is acceptable.

² Although this device is suitable, it is not commercially made. It may also require retrofitting to accommodate ZHE devices.

TABLE 3.—SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS

Company	Location	Model No
Associated Design & Manufacturing Co.	Alexandria, VA, (703) 549-5993.	3740-ZHB, Gas Pressure Device.
Millipore Corp.	Bedford, MA, (800) 225-3384.	501 P581 C5, Gas Pressure Device.
Analytical Testing & Consulting Services, Inc.	Warrington, PA, (215) 343-4430.	Co2, Mechanical Pressure Device.

TABLE 4.—SUITABLE FILTER HOLDERS¹

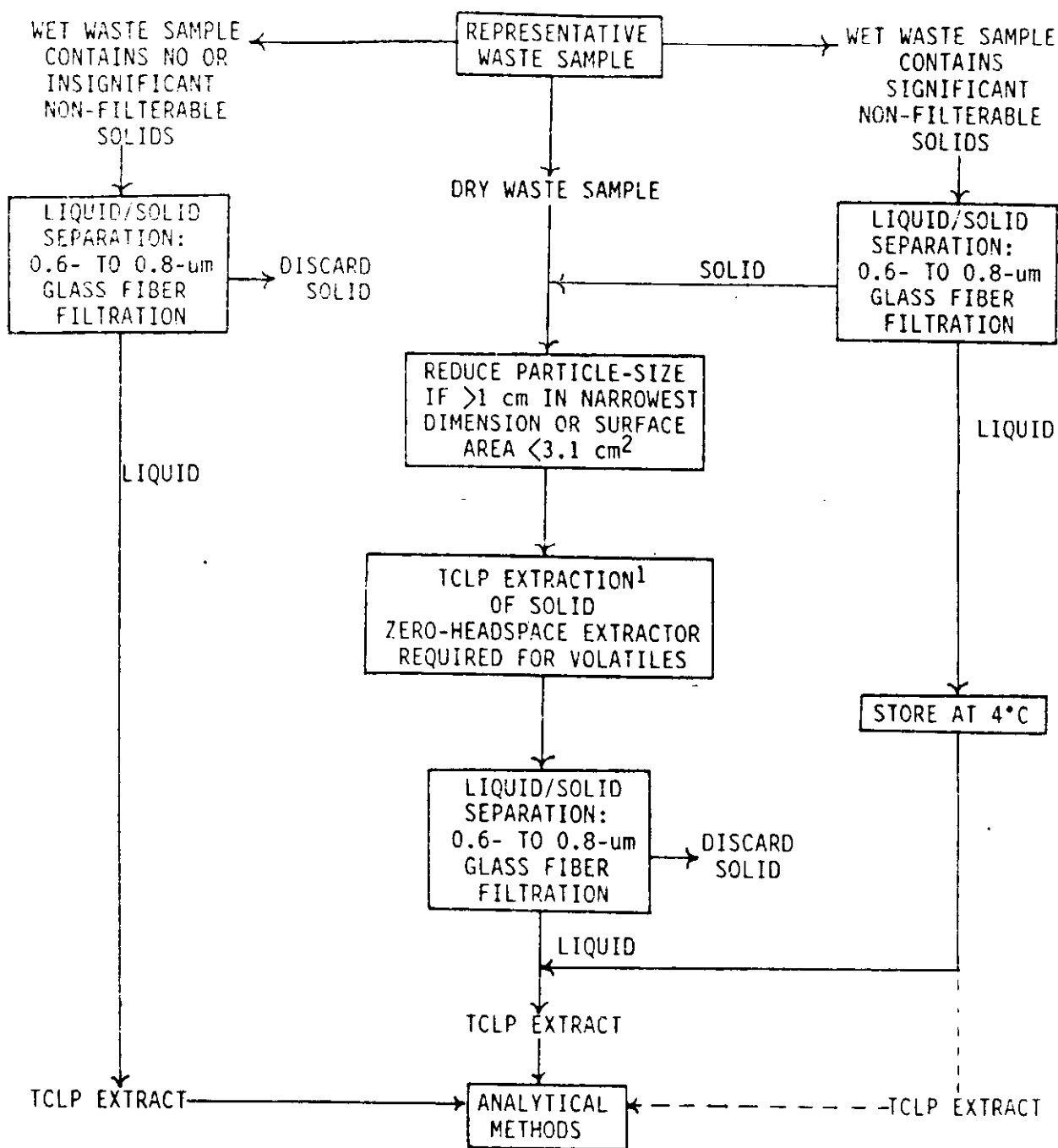
Company	Location	Model	Size
Nuclepore Corp.	Pleasanton, CA, (909) 832-7711.	425210	142 mm
		410100	47 mm
Micro Filtration Systems	Dublin, CA, (415) 828-6010.	302400	142 mm
Millipore Corp.	Bedford, MA, (800) 225-3384.	YT30142H/W	142 mm
		XX1004700	47 mm

¹ Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic contaminants are of concern. The 142 mm size filter holder is recommended.

TABLE 5.—SUITABLE FILTER MEDIA

Company	Location	Model	Pore Size
Whatman Laboratory Products, Inc.	Clifton, NJ, (201) 773-5200.	GFF	0.7

¹ Nominal pore size.



¹The extraction fluid employed is a function of the alkalinity of the solid phase of the waste.

FIGURE 1: TCLP FLOWCHART

[Appendix I]

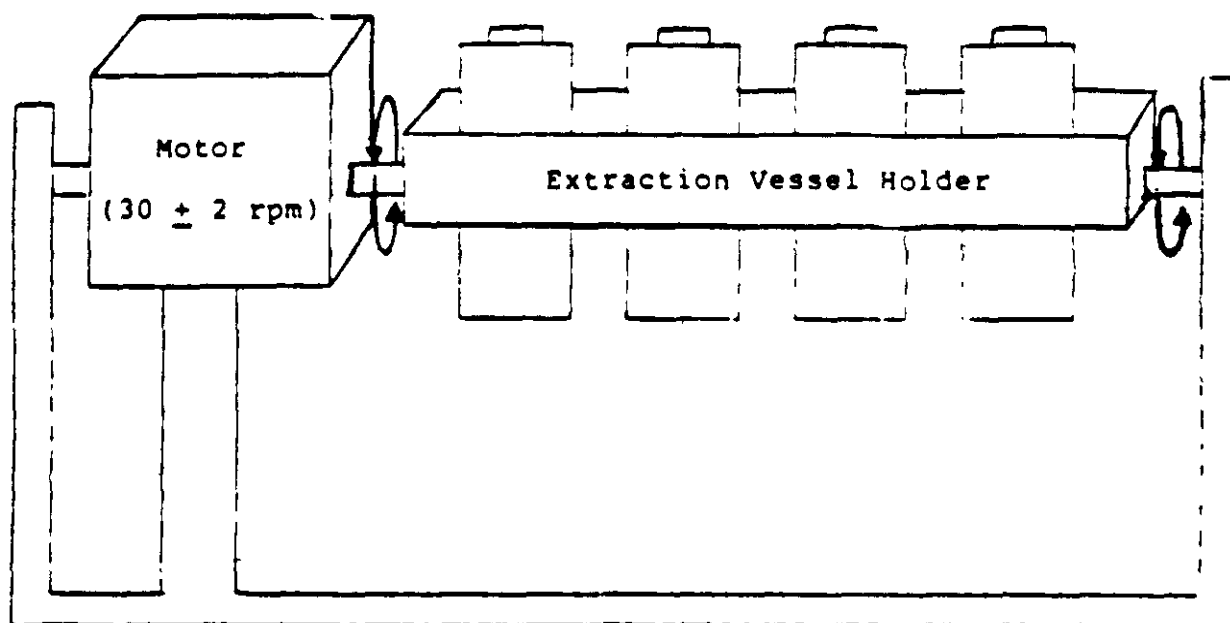


Figure 2: Rotary Agitation

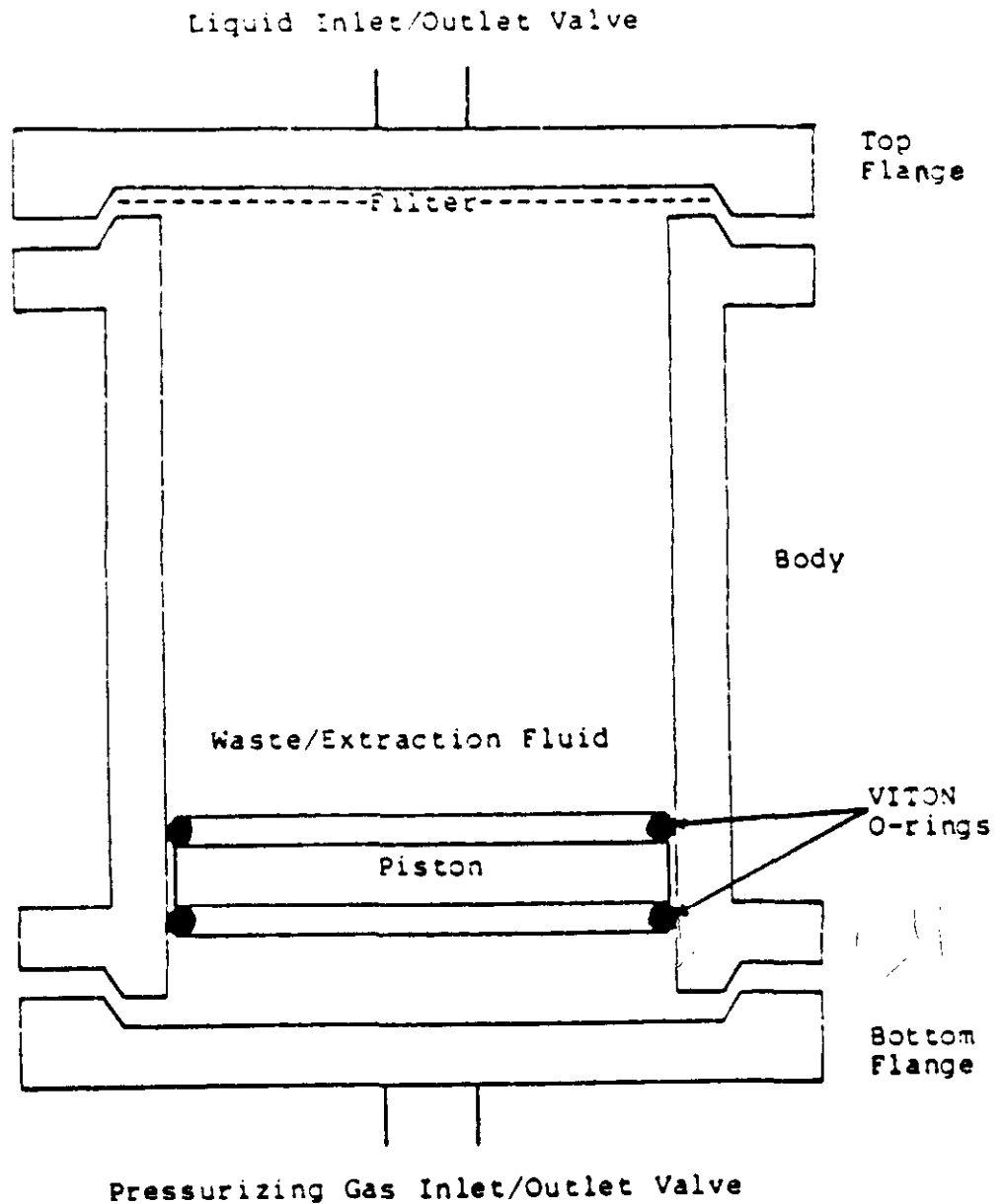


Figure 3: Zero-Headspace Extraction Vessel

[Appendix I]

APPENDIX II TO PART 268—TREATMENT STANDARDS (AS CONCENTRATIONS IN THE TREATMENT RESIDUAL EXTRACT)

[Appendix II added by 51 FR 40636, November 7, 1986]

(Note: The technologies shown are the basis of the treatment standards. They are not required to be used in meeting the treatment standards.)

Constituents of F001-F005 Spent Solvent Wastes	Waste Treatability Groups For F001-F005 Spent Solvent Wastes (mg/l)			
	Wastewater	Technology Basis ¹	Wastewater Generated by Pharmaceutical Plant ²	All Other ³
Acetone	0.05	SS		0.59
n-Butyl Alcohol	5.00	SS		5.00
Carbon disulfide	1.05	SS		4.81
Carbon tetrachloride	0.05	B		0.96
Chlorobenzene	0.15	B&AC		0.05
Cresols (arabic acid)	2.82	AC		0.75
Dichloroethane	0.125	SS		0.75
1,2-Dichlorobenzene	0.65	B&AC		0.125
Ethyl acetate	0.05	SS		0.75
Ethylbenzene	0.05	B		0.053
Ethyl ether	0.05	SS		0.75
Isobutanol	5.00	SS		5.00
Methanol	0.05	SS		0.75
Methylene chloride	0.20	B	12.7	0.96
Methyl ethyl ketone	0.05	SS		0.75
Methyl isobutyl ketone	0.05	SS		0.33
Nitrobenzene	0.65	SS&AC		0.125
Pyridine	1.12	B&AC		0.13
Tetrachloroethylene	0.15	B		0.05
Toluene	1.12	B&AC		0.33
1,1,1-Trichloroethane	1.05	SS		0.41
1,1,2-Trichloro-1,2,2-trifluoroethane	1.05	SS		0.96
Trichloroethylene	0.062	B&AC		0.091
Trichlorofluoromethane	0.05	B		0.96
Xylene	0.05	AC		0.15

¹ In some instances other technologies achieved somewhat lower treatment values but waste characterization data were insufficient to identify separate treatability groups. Refer to the BtuAT background document for a detailed explanation of the determination of the treatment standards.

SS = steam stripping

B = biological treatment

AC = activated carbon

² Wastewaters generated by pharmaceutical plants must be treated to the standards given for all other wastewaters except in the case of methylene chloride.

³ The treatment standards in this treatability group are based on incineration.

Appendix III to Part 268—List of Halogenated Organic Compounds Regulated Under § 268.32

[Appendix III added by 52 FR 25787, July 8, 1987]

In determining the concentration of HOCs in a hazardous waste for purposes of the § 268.32 land disposal prohibition, EPA has defined the HOCs that must be included in the calculation as any compounds having a carbon-halogen bond which are listed in this Appendix (see § 268.2). Appendix III to Part 268 consists of the following compounds:

Volatiles

Bromodichloromethane
Bromomethane
Carbon Tetrachloride
Chlorobenzene
2-Chloro-1,3-butadiene
Chlorodibromomethane
Chloroethane
2-Chloroethyl vinyl ether
Chloroform
Chloromethane
3-Chloropropene
1,2-Dibromo-3-chloropropane
1,2-Dibromomethane

Dibromomethane
Trans-1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethylene
Trans-1,2-Dichloroethene
1,2-Dichloropropane
Trans-1,3-Dichloropropene
cis-1,3-Dichloropropene
Iodomethane
Methylene chloride
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Tribromomethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichloromonofluoromethane
1,2,3-Trichloropropane
Vinyl chloride

Semivolatiles

Bis(2-chloroethoxy)ethane
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl) ether
p-Chloroaniline
Chlorobenzilate

p-Chloro-m-cresol
2-Chloronaphthalene
2-Chlorophenol
3-Chloropropionitrile
m-Dichlorobenzene
o-Dichlorobenzene
p-Dichlorobenzene
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachloropropene
Hexachloropropene
4,4'-Methylenebis(2-chloroaniline)
Pentachlorobenzene
Pentachloroethane
Pentachloronitrobenzene
Pentachlorophenol
Pronamide
1,2,4,5-Tetrachlorobenzene
2,3,4,6-Tetrachlorophenol
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Tris(2,3-dibromopropyl)phosphate

[Appendix III]

Organochlorine Pesticides

Aldrin
alpha-BHC
beta-BHC
delta-BHC
gamma-BHC
Chlordane
DDD
DDE
DDT
Dieldrin
Endosulfan I
Endosulfan II
Endrin
Endrin aldehyde

Heptachlor
Heptachlor epoxide
Isodrin
Kepone
Methoxychlor
Toxaphene

Phenoxyacetic Acid Herbicides

2,4-Dichlorophenoxyacetic acid
Silvex
2,4,5-T

PCBs

Aroclor 1016
Aroclor 1221

Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
PCBs not otherwise specified

Dioxins and Furans

Hexachlorodibenzo-p-dioxins
Hexachlorodibenzofuran
Pentachlorodibenzo-p-dioxins
Pentachlorodibenzofuran
Tetrachlorodibenzo-p-dioxins
Tetrachlorodibenzofuran
2,3,7,8-Tetrachlorodibenzo-p-dioxin

[Appendix III]

Part 261, App. I

§ 261.33 Discarded commercial chemical products, off-specification species, container residues and spill residues thereof.

The following materials or items are hazardous wastes if and when they are discarded or intended to be discarded unless they are excluded under §§ 260.20 and 260.22 and listed in Appendix IX.

(f) * * *

Hazardous waste No.	Substance
U242	Pentachlorophenol.
U242	Phenol, pentachloro-
U212	Phenol, 2,3,4,6-tetrachloro-
U212	Phenol, 2,4,5-trichloro-
U230	Phenol, 2,4,6-trichloro-
U231	Propionic acid, 2-(2,4,5-trichlorophenoxy)-
U233	Silver.
U232	2,4,5-T.
U212	2,3,4,6-Tetrachlorophenol.
U230	2,4,5-Trichlorophenol.
U231	2,4,6-Trichlorophenol.
U230	2,4,5-Trichlorophenoxyacetic acid.

APPENDIX I—REPRESENTATIVE SAMPLING METHODS

The methods and equipment used for sampling waste materials will vary with the form and consistency of the waste materials to be sampled. Samples collected using the sampling protocols listed below, for sampling waste with properties similar to the indicated materials, will be considered by the Agency to be representative of the waste.

Extremely viscous liquid—ASTM Standard D140-70 Crushed or powdered material—ASTM Standard D346-75 Soil or rock-like material—ASTM Standard D420-69 Soil-like material—ASTM Standard D1452-65 Fly Ash-like material—ASTM Standard D2234-76 [ASTM Standards are available from ASTM, 1916 Race St., Philadelphia, PA 19103]

Containerized liquid wastes—"COLIWASA" described in "Test Methods for the Evaluation of Solid Waste, Physical/Chemical

40 CFR Ch. I (7-1-85 Edition)

Methods," * U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C. 20460. [Copies may be obtained from Solid Waste Information, U.S. Environmental Protection Agency, 26 W. St. Clair St., Cincinnati, Ohio 45268] Liquid waste in pits, ponds, lagoons, and similar reservoirs.—"Pond Sampler" described in "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods," *

This manual also contains additional information on application of these protocols.

APPENDIX II—EP TOXICITY TEST PROCEDURES

A. Extraction Procedure (EP)

1. A representative sample of the waste to be tested (minimum size 100 grams) shall be obtained using the methods specified in Appendix I or any other method capable of yielding a representative sample within the meaning of Part 260. [For detailed guidance on conducting the various aspects of the EP see "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods" (incorporated by reference, see § 260.11).]

2. The sample shall be separated into its component liquid and solid phases using the method described in "Separation Procedure" below. If the solid residue * obtained using this method totals less than 0.5% of the original weight of the waste, the residue can be discarded and the operator shall treat the liquid phase as the extract and proceed immediately to Step 8.

3. The solid material obtained from the Separation Procedure shall be evaluated for its particle size. If the solid material has a surface area per gram of material equal to, or greater than, 3.1 cm² or passes through a 9.5 mm (0.375 inch) standard sieve, the operator shall proceed to Step 4. If the surface area is smaller or the particle size larger than specified above, the solid material shall be prepared for extraction by crushing, cutting or grinding the material so that

* These methods are also described in "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA 600/2-80-018, January 1980.

* The percent solids is determined by drying the filter pad at 80°C until it reaches constant weight and then calculating the percent solids using the following equation:
Percent solids =

$$\frac{(\text{weight of pad} + \text{solid}) - (\text{tare weight of pad})}{\text{initial weight of sample}} \times 100$$

it passes through a 9.5 mm (0.375 inch) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described below.

4. The solid material obtained in Step 3 shall be weighed and placed in an extractor with 16 times its weight of deionized water. Do not allow the material to dry prior to weighing. For purposes of this test, an acceptable extractor is one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid but also insure that all sample surfaces are continuously brought into contact with well mixed extraction fluid.

5. After the solid material and deionized water are placed in the extractor, the operator shall begin agitation and measure the pH of the solution in the extractor. If the pH is greater than 5.0, the pH of the solution shall be decreased to 5.0 ± 0.2 by adding 0.5 N acetic acid. If the pH is equal to or less than 5.0, no acetic acid should be added. The pH of the solution shall be monitored, as described below, during the course of the extraction and if the pH rises above 5.2, 0.5N acetic acid shall be added to bring the pH down to 5.0 ± 0.2 . However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture shall be agitated for 24 hours and maintained at 20°-40°C (68°-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123 or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed:

(a) A pH meter shall be calibrated in accordance with the manufacturer's specifications.

(b) The pH of the solution shall be checked and, if necessary, 0.5N acetic acid shall be manually added to the extractor until the pH reaches 5.0 ± 0.2 . The pH of the solution shall be adjusted at 15, 30 and 60 minute intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5N pH units.

(c) The adjustment procedure shall be continued for at least 6 hours.

(d) If at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH shall be adjusted to 5.0 ± 0.2 and the extraction continued for an additional four hours, during which the pH shall be adjusted at one hour intervals.

6. At the end of the 24 hour extraction period, deionized water shall be added to

the extractor in an amount determined by the following equation:

$$V = (20 \times W) - 16(W) - A$$

V = ml deionized water to be added

W = weight in grams of solid charged to extractor

A = ml of 0.5N acetic acid added during extraction

7. The material in the extractor shall be separated into its component liquid and solid phases as described under "Separation Procedure."

8. The liquids resulting from Steps 2 and 7 shall be combined. This combined liquid (or the waste itself if it has less than ¼ percent solids, as noted in step 2) is the extract and shall be analyzed for the presence of any of the contaminants specified in Table I of § 261.24 using the Analytical Procedures designated below.

Separation Procedure

Equipment: A filter holder, designed for filtration media having a nominal pore size of 0.45 micrometers and capable of applying a 5.3 kg/cm² (75 psi) hydrostatic pressure to the solution being filtered, shall be used. For mixtures containing nonabsorptive solids, where separation can be effected without imposing a 5.3 kg/cm² pressure differential, vacuum filters employing a 0.45 micrometers filter media can be used. (For further guidance on filtration equipment or procedures see "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" incorporated by reference, see § 260.11). Procedure:¹

(1) Following manufacturer's directions, the filter unit shall be assembled with a filter bed consisting of a 0.45 micrometer filter membrane. For difficult or slow to filter mixtures a prefilter bed consisting of the following prefilters in increasing pore size (0.65 micrometer membrane, fine glass

¹This procedure is intended to result in separation of the "free" liquid portion of the waste from any solid matter having a particle size >0.45 µm. If the sample will not filter, various other separation techniques can be used to aid in the filtration. As described above, pressure filtration is employed to speed up the filtration process. This does not alter the nature of the separation. If liquid does not separate during filtration, the waste can be centrifuged. If separation occurs during centrifugation, the liquid portion (centrifugate) is filtered through the 0.45 µm filter prior to becoming mixed with the liquid portion of the waste obtained from the initial filtration. Any material that will not pass through the filter after centrifugation is considered a solid and is extracted.

fiber prefilter, and coarse glass fiber prefilter) can be used.

(ii) The waste shall be poured into the filtration unit.

(iii) The reservoir shall be slowly pressurized until liquid begins to flow from the filtrate outlet at which point the pressure in the filter shall be immediately lowered to 10-15 psig. Filtration shall be continued until liquid flow ceases.

(iv) The pressure shall be increased stepwise in 10 psi increments to 75 psig and filtration continued until flow ceases or the pressurizing gas begins to exit from the filtrate outlet.

(v) The filter unit shall be depressurized, the solid material removed and weighed and then transferred to the extraction apparatus, or, in the case of final filtration prior to analysis, discarded. Do not allow the material retained on the filter pad to dry prior to weighing.

(vi) The liquid phase shall be stored at 4°C for subsequent use in Step 8.

B. Structural Integrity Procedure

Equipment: A Structural Integrity Tester having a 3.18 cm (1.25 in.) diameter hammer weighing 0.33 kg (0.73 lbs.) and having a free fall of 15.24 cm (6 in.) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet the specifications shown in Figure 1.

Procedure

1. The sample holder shall be filled with the material to be tested. If the sample of waste is a large monolithic block, a portion shall be cut from the block having the dimensions of a 3.3 cm (1.3 in.) diameter x 7.1 cm (2.8 in.) cylinder. For a fixated waste, samples may be cast in the form of a 3.3 cm (1.3 in.) diameter x 7.1 cm (2.8 in.) cylinder for purposes of conducting this test. In such cases, the waste may be allowed to cure for 30 days prior to further testing.

2. The sample holder shall be placed into the Structural Integrity Tester, then the hammer shall be raised to its maximum height and dropped. This shall be repeated fifteen times.

3. The material shall be removed from the sample holder, weighed, and transferred to the extraction apparatus for extraction.

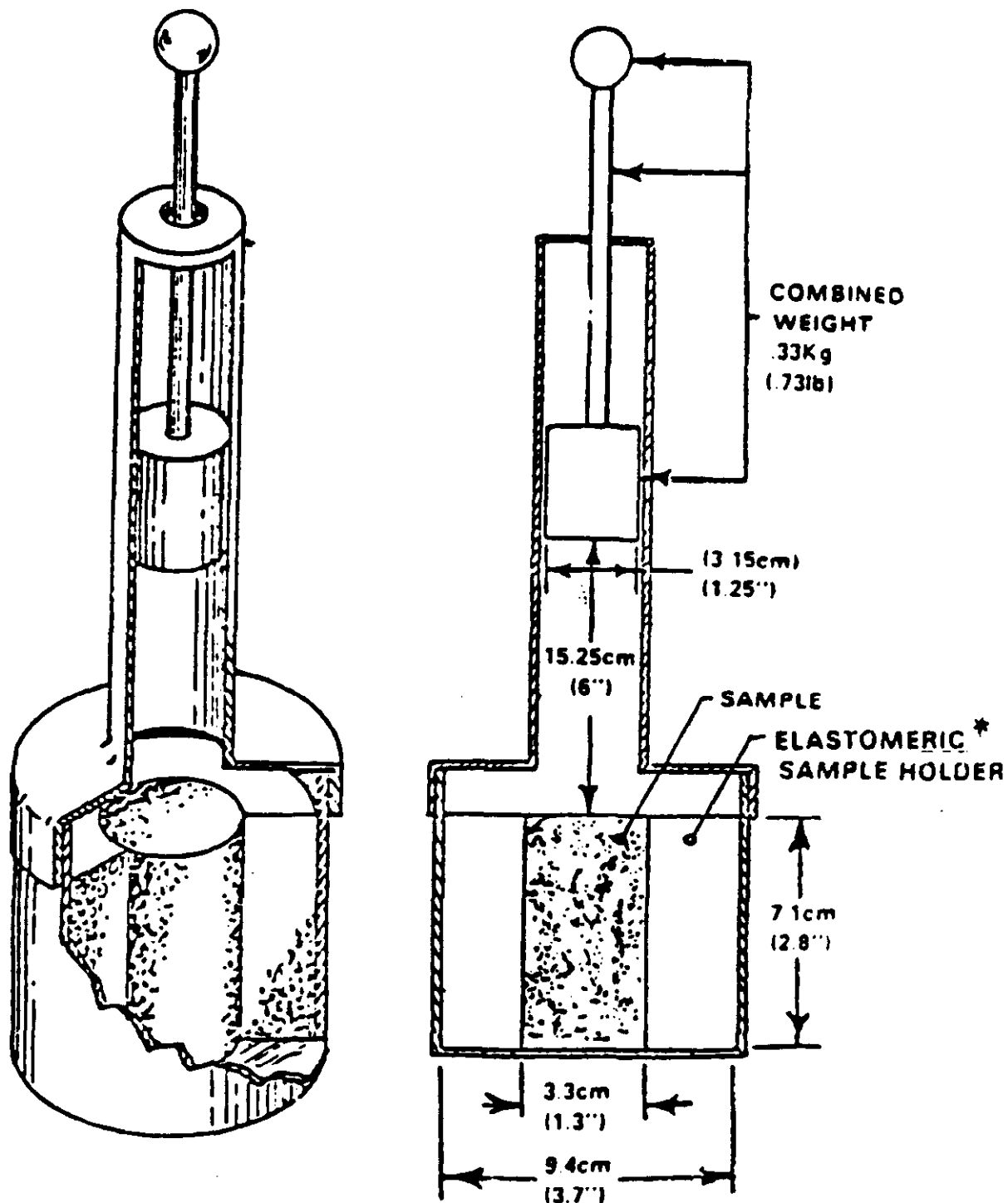
Analytical Procedures for Analyzing Extract Contaminants

The test methods for analyzing the extract are as follows:

1. For arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, endrin, lindane, methoxychlor, toxaphene, 2,4-D[2,4-dichlorophenoxyacetic acid] or 2,4,5-TP [2,4,5-trichlorophenoxypropionic acid]: "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods" (incorporated by reference, see § 260.11).

2. [Reserved]

For all analyses, the methods of standard addition shall be used for quantification of species concentration.



*ELASTOMERIC SAMPLE HOLDER FABRICATED OF MATERIAL FIRM ENOUGH TO SUPPORT THE SAMPLE

Figure 1
COMPACTION TESTER

TEMPERATURE

Method 170.1 (Thermometric)

STORET NO. 00010

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
 - 2.1 Temperature measurements may be made with any good grade of mercury-filled or dial type centigrade thermometer, or a thermistor.
3. Comments
 - 3.1 Measurement device should be routinely checked against a precision thermometer certified by the National Bureau of Standards.
4. Precision and Accuracy
 - 4.1 Precision and accuracy for this method have not been determined.
5. Reference
 - 5.1 The procedure to be used for this determination is found in:
Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 125,
Method 212 (1975).

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ARSENIC

Method 206.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01002

Dissolved 01000

Suspended 01001

Optimum Concentration Range: 5–100 ug/l

Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/l).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3 , 2ml of 30% H_2O_2 and 2ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace.

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NOTE: If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1100°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 μl injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as $\mu\text{g/l}$.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent containing 15 $\mu\text{g/l}$ and spiked with concentrations of 2, 10 and 25 $\mu\text{g/l}$, recoveries of 85%, 90% and 88% were obtained respectively. The relative standard deviation at these concentrations levels were $\pm 8.8\%$, $\pm 8.2\%$, $\pm 5.4\%$ and $\pm 8.7\%$, respectively.
2. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 20, 50 and 100 $\mu\text{g As/l}$, the standard deviations were ± 0.7 , ± 1.1 and ± 1.6 respectively. Recoveries at these levels were 105%, 106% and 101%, respectively.

ARSENIC

Method 206.3 (Atomic Absorption—gaseous hydride)

STORET NO. Total 01002

Dissolved 01000

Suspended 01001

1. Scope and Application
 - 1.1 The gaseous hydride method determines inorganic arsenic when present in concentrations at or above 2 ug/l. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.
2. Summary of Method
 - 2.1 Arsenic in the sample is first reduced to the trivalent form using SnCl_2 and converted to arsine, AsH_3 , using zinc metal. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2–20 ug/l. The 193.7 nm wavelength line is used.
3. Comments
 - 3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.
 - 3.2 Organic forms of arsenic must be converted to inorganic compounds and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in Method 206.5 (Standard Methods, 14th Edition, Method 404B, p. 285, Procedure 4.a) has been found suitable.
 - 3.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
 - 3.4 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
 - 3.5 Data to be entered into STORET must be reported as ug/l.
4. Precision and Accuracy
 - 4.1 Ten replicate solutions of o-arsenilic acid at the 5, 10 and 20 ug/l level were analyzed by a single laboratory. Standard deviations were ± 0.3 , ± 0.9 and ± 1.1 with recoveries of 94, 93 and 85%, respectively. (Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA., vol 65, p 731, Nov., 1973.)

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5. References

- 5.1. Except for the perchloric acid step, the procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 14th Edition, p159, Method 301A(VII),(1975)

OIL AND GREASE, TOTAL, RECOVERABLE

Method 413.1 (Gravimetric, Separatory Funnel Extraction)

STORET NO. 00556

1. Scope and Application
 - 1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
 - 1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation.
 - 1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.
 - 1.4 The method covers the range from 5 to 1000 mg/l of extractable material.
2. Summary of Method
 - 2.1 The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.
3. Definitions
 - 3.1 The definition of oil and grease is based on the procedure used. The nature of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.
4. Sampling and Storage
 - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.
 - 4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.
5. Apparatus
 - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
 - 5.2 Vacuum pump, or other source of vacuum.
 - 5.3 Flask, boiling, 125 ml (Corning No. 4100 or equivalent).
 - 5.4 Distilling head, Claisen or equivalent.
 - 5.5 Filter paper, Whatman No. 40, 11 cm.
6. Reagents
 - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.

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- 6.2 Fluorocarbon-113, (1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.
- 6.3 Sodium sulfate, anhydrous crystal.
7. Procedure
- 7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.
- 7.2 Pour the sample into a separatory funnel.
- 7.3 Tare a boiling flask (pre-dried in an oven at 103°C and stored in a desiccator).
- 7.4 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate, and filter the solvent layer into the flask through a funnel containing solvent moistened filter paper.
- NOTE:** An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.
- 7.5 Repeat (7.4) twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.
- 7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10–20 ml solvent and collect the rinsings in the flask.
- 7.7 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each set of samples.
- 7.8 When the temperature in the distilling head reaches 50°C or the flask appears dry remove the distilling head. Sweep out the flask for 15 seconds with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.
- 7.9 Cool the boiling flask in a desiccator for 30 minutes and weigh.
8. Calculation
- 8.1 $\text{mg/l total oil and grease} = \frac{R - B}{V}$

where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams.

B = blank determination, residue of equivalent volume of extraction solvent, in milligrams.

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

- 9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 12.6 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 93% with a standard deviation of ± 0.9 mg/l.

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PHOSPHORUS, TOTAL

Method 365.4 (Colorimetric, Automated, Block Digester AA II)

STORET NO. 00665

1. Scope and Application
 - 1.1 This method covers the determination of total phosphorus in drinking water, surface water and domestic and industrial wastes. The applicable range of this method is 0.01 to 20 mg P/l.
2. Summary of Method
 - 2.1 The sample is heated in the presence of sulfuric acid, K_2SO_4 and $HgSO_4$ for two and one half hours. The residue is cooled, diluted to 25 ml and placed on the AutoAnalyzer for phosphorus determination.
3. Sample Handling and Preservation
 - 3.1 Sample containers may be of plastic material, such as a cubitainer, or of Pyrex glass.
 - 3.2 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 ml of conc. H_2SO_4 per liter and refrigeration at 4°C.
4. Apparatus
 - 4.1 Block Digester BD-40
 - 4.2 Technicon Method No. 327-74W for Phosphorus
5. Reagents
 - 5.1 Mercuric sulfate: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10 conc. H_2SO_4 ; 40 ml distilled water) and dilute to 100 ml with distilled water.
 - 5.2 Digestion solution: (Sulfuric acid-mercuric sulfate-potassium sulfate solution): Dissolve 133 g of K_2SO_4 in 600 ml of distilled water and 200 ml of conc. H_2SO_4 . Add 25 ml of mercuric sulfate solution (5.1) and dilute to 1 liter.
 - 5.3 Sulfuric acid solution (0.72 N): Add 20 ml of conc. sulfuric acid to 800 of distilled water, mix and dilute to 1 liter.
 - 5.4 Molybdate/antimony solution: Dissolve 8 g of ammonium molybdate and 0.2 g of antimony potassium tartrate in about 800 ml of distilled water and dilute to 1 liter.
 - 5.5 Ascorbic acid solution: Dissolve 60 g of ascorbic acid in about 600 ml of distilled water. Add 2 ml of acetone and dilute to 1 liter.
 - 5.6 Diluent water: Dissolve 40 g of NaCl in about 600 ml of distilled water and dilute to 1 liter.
 - 5.7 Sulfuric acid solution, 4%: Add 40 ml of conc. sulfuric acid to 800 ml of ammonia-free distilled water, cool and dilute to 1 liter.
6. Procedure
 - Digestion
 - 6.1 To 20 or 25 ml of sample, add 5 ml of digestion solution and mix. (Use a vortex mixer).
 - 6.2 Add 4-8 Teflon boiling chips. Too many boiling chips will cause the sample to boil over.

Pending approval for NPDES and Section 304(h), CWA
Issued 1974

- 6.3 With Block Digestor in manual mode set low and high temperature at 160°C and preheat unit to 160°C. Place tubes in digestor and switch to automatic mode. Set low temperature timer for 1 hour. Reset high temperature to 380°C and set timer for 2 1/2 hours.
- 6.4 Cool sample and dilute to 25 ml with distilled water. If TKN is determined the sample should be diluted with ammonia-free water.

Colorimetric Analysis

- 6.4.1 Check the level of all reagent containers to ensure an adequate supply.
 - 6.4.2 Excluding the molybdate/antimony line, place all reagent lines in their respective containers, connect the sample probe to the Sampler IV and start the proportioning pump.
 - 6.4.3 Flush the Sampler IV wash receptacle with about 25 ml of 4% sulfuric acid (5.7).
 - 6.4.4 When reagents have been pumping for at least five minutes, place the molybdate/antimony line in its container and allow the system to equilibrate.
 - 6.4.5 After a stable baseline has been obtained, start the sampler.
7. Calculations
 - 7.1 Prepare a standard curve by plotting peak heights of processed standards against concentration values. Compute concentrations by comparing sample peak heights with the standard curve.
 8. Precision and Accuracy
 - 8.1 In a single laboratory (EMSL) using sewage sample containing total P at levels of 0.23, 1.33, and 2.0, the precision was ± 0.01 , ± 0.04 , and ± 0.06 , respectively.
 - 8.2 In a single laboratory (EMSL) using sewage samples of concentration 1.84 and 1.89, the recoveries were 95 and 98%, respectively.

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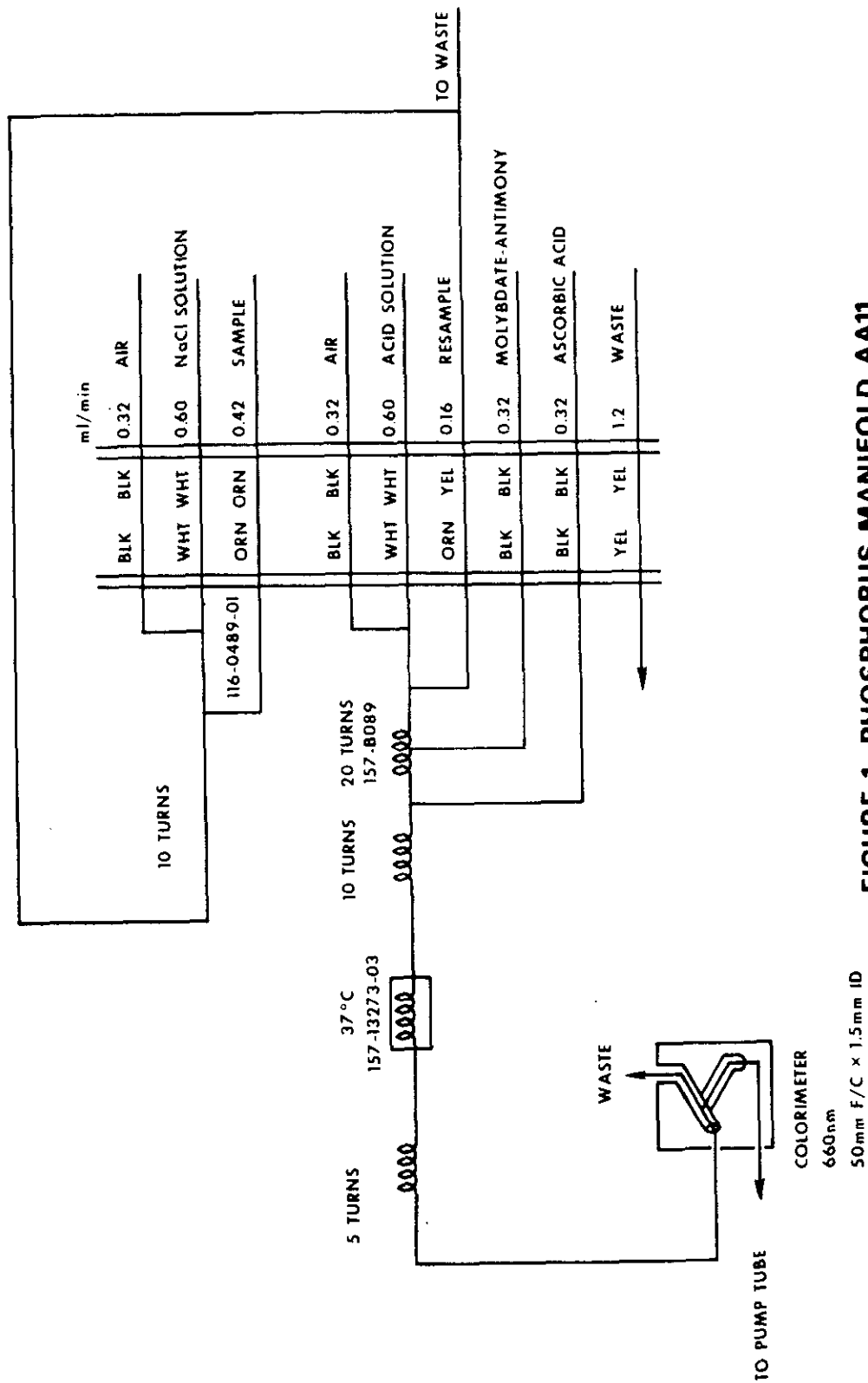


FIGURE 1. PHOSPHORUS MANIFOLD AA11

ARSENIC

Method 206.4 (Spectrophotometric-SDDC)

STORET NO. 01002
Inorganic, Dissolved 00095
Inorganic, Total 00997
Inorganic, Suspended 00996

1. Scope and Application
 - 1.1 The silver diethyldithiocarbamate method determines inorganic arsenic when present in concentrations at or above 10 ug/l. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver. Domestic and industrial wastes may also be analyzed after digestion (see 3.3).
 - 1.2 Difficulties may be encountered with certain industrial waste materials containing volatile substances. High sulfur content of wastes may exceed removal capacity of the lead acetate scrubber.
2. Summary of Method
 - 2.1 Arsenic in the sample is reduced to arsine, AsH_3 , in acid solution in a hydrogen generator. The arsine is passed through a scrubber to remove sulfide and is absorbed in a solution of silver diethyldithiocarbamate dissolved in pyridine. The red complex thus formed is measured in a spectrophotometer at 535 nm.
3. Comments
 - 3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.
 - 3.2 It is essential that the system be airtight during evolution of the arsine, to avoid losses.
 - 3.3 If concentration of the sample and/or oxidation of any organic matter is required, refer to Method 206.5. [Standard Methods, 14th Edition, Method 404B, p. 284, Procedure 4.a (1975)]. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
 - 3.3.1 Since nitric acid gives a negative interference in this test, use sulfuric acid as a preservative if only inorganic arsenic is being measured.
 - 3.4 1-Ephedrine in chloroform has been found to be a suitable solvent for silver diethyldithiocarbamate if the analyst finds the odor of pyridine objectionable [Anal. Chem. 45, 1786 (1973)].
 - 3.5 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

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4. Precision and Accuracy

4.1 In a round-robin study reported by Standard Methods a synthetic unknown sample containing 40 $\mu\text{g}/\text{l}$, as As, with other metals was analyzed in 46 laboratories. Relative standard deviation was $\pm 13.8\%$ and relative error was 0%.

5. Reference

5.1 The procedure to be used for this determination is found in:
Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 283,
Method 404A (1975).

ARSENIC

Method 206.5 (Sample Digestion Prior to Total Arsenic Analysis by Silver Diethyldithiocarbamate or Hydride Procedures)

1. Scope and Application:
 - 1.1 Both the silver diethyldithiocarbamate spectrophotometric method and the AA hydride procedure measure inorganic arsenic. Therefore, if either of these procedures are being employed for the purpose of measuring total arsenic (inorganic plus organic), all organically bound arsenic must first be converted to an inorganic form prior to the analytical determination. This may be accomplished with $\text{H}_2\text{SO}_4\text{-HNO}_3$.
2. Procedure
 - 2.1 To a suitable sample containing from 2 to 30 μg of arsenic, add 7 ml (1 + 1) H_2SO_4 and 5 ml conc HNO_3 . Evaporate the sample to SO_3 fumes. Caution: If the sample chars, stop the digestion immediately, cool and add additional conc HNO_3 . Continue digestion adding additional conc HNO_3 as necessary.
 - 2.2 If the sample remains colorless, or straw-yellow during evolution of SO_3 fumes, the digestion is complete.
 - 2.3 Cool the digested sample, add about 25 ml distilled water, and again evaporate to SO_3 fumes to expel oxides of nitrogen.
 - 2.4 The sample is now ready for analysis using either the hydride or spectrophotometric procedure.
3. Interferences
 - 3.1 All traces of nitric acid must be removed before either the spectrophotometric or the hydride procedures are applied. Oxides of nitrogen should be expelled by taking the sample to fumes of SO_3 .
4. Notes
 - 4.1 The digestion step may be carried out in a flask on a hot-plate or in a Kjeldahl apparatus. This digestion step may also be used, in effect, to concentrate the sample, inasmuch as any size volume may be processed.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p285, method 404B, step 4a, 14th Edition (1975).

RESIDUE, NON-FILTERABLE

Method 160.2 (Gravimetric, Dried at 103–105°C)

STORET NO. 00530

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The practical range of the determination is 4 mg/l to 20,000 mg/l.
2. Summary of Method
 - 2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103–105°C.
 - 2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
 - 3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103–105°C.
4. Sample Handling and Preservation
 - 4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
 - 4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
 - 5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
 - 5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.
6. Apparatus
 - 6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.

NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
 - 6.2 Filter support: filtering apparatus with reservoir and a coarse (40–60 microns) fritted disc as a filter support.

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NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

- 6.3 Suction flask.
 - 6.4 Drying oven, 103–105°C.
 - 6.5 Desiccator.
 - 6.6 Analytical balance, capable of weighing to 0.1 mg.
 - 7. Procedure
 - 7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103–105°C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.
 - 7.2 Selection of Sample Volume

For a 4.7 cm diameter filter, filter 100 ml of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 ml/cm² of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

NOTE: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five ml increments for timing are suggested. Continue to record the time and volume increments until filtration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.
 - 7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.
 - 7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.
 - 7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.
- NOTE:** Total volume of wash water used should equal approximately 2 ml per cm². For a 4.7 cm filter the total volume is 30 ml.

- 7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103–105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).
8. Calculations
- 8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A - B) \times 1,000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = ml of sample filtered

9. Precision and Accuracy
- 9.1 Precision data are not available at this time.
- 9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

pH

Method 150.1 (Electrometric)

STORET NO.

Determined on site 00400

Laboratory 00403

1. **Scope and Application**
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).
2. **Summary of Method**
 - 2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. **Sample Handling and Preservation**
 - 3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
 - 3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. **Interferences**
 - 4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
 - 4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
 - 4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
 - 4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. **Apparatus**
 - 5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

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- 5.2 Glass electrode.
- 5.3 Reference electrode—a calomel, silver-silver chloride or other reference electrode of constant potential may be used.
NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.
- 5.4 Magnetic stirrer and Teflon-coated stirring bar.
- 5.5 Thermometer or temperature sensor for automatic compensation.
- 6. **Reagents**
 - 6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.
 - 6.1.1 Preparation of reference solutions from these salts require some special precautions and handling⁽¹⁾ such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.
 - 6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.
- 7. **Calibration**
 - 7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.
 - 7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.
 - 7.2.1 Various instrument designs may involve use of a “balance” or “standardize” dial and/or a slope adjustment as outlined in the manufacturer’s instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.
- 8. **Procedure**
 - 8.1 Standardize the meter and electrode system as outlined in Section 7.
 - 8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.
 - 8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (<0.1 pH) readings.
 - 8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual

⁽¹⁾National Bureau of Standards Special Publication 260.

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

- 8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.
- 8.5 For acid rain samples it is most important that the magnetic stirrer is not used. Instead, swirl the sample gently for a few seconds after the introduction of the electrode(s). Allow the electrode(s) to equilibrate. The air-water interface should not be disturbed while measurement is being made. If the sample is not in equilibrium with the atmosphere, pH values will change as the dissolved gases are either absorbed or desorbed. Record sample pH and temperature.
9. Calculation
 - 9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.
10. Precision and Accuracy
 - 10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as	
		Bias, %	Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

- 10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ± 0.1 .

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293-65, p 178 (1976).
3. Peden, M. E. and Skowron, L. M., Ionic Stability of Precipitation Samples, Atmospheric Environment, Vol. 12, pp. 2343-2349, 1978.